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THE EFFECT OF GRINDING ON THE ACIDULATION OF PHOSPHATE ROCK

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by

Robert Richard Rounsley

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Dean of Graduate College

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ABSTRACT

An investigation was undertaken to determine the effect of grinding on the acidulation of phosphate rock. Bench-scale work was carried out in a one quart, laboratory ball mill made of stainless steel. The mill was equipped with a heating chamber so that the material could also be dried in the mill.

The results from this work indicated that a normal superphosphate product suitable for commercial use could be obtained within an hour after the addition of the first acid. The product had low moisture and low free acid contents, and under suitable conditions, granular form. The mixing action of the balls resulted in good heat transfer during drying with little danger of overheating the product. Consequently, the drying air temperature had little effect on the product except in the rate of production. The reaction was sufficiently rapid in the mill so that no preliminary grinding period was necessary before the drying operation was started. Low acidulation ratios resulted in low conversions as in any normal superphosphate process. Low acid concentrations were more conducive to a rapid reaction between the rock and acid. Below an acid strength of about 55 per cent, however, there was no further advantage in dilution.

The favorable results of the bench-scale work led to the construction of a pilot plant to determine whether the process could be carried out on a larger scale and on a continuous basis. The process was built around a heated tube mill with a stainless steel lining and a feeding mechanism.

Heating was indirect. The acid and rock were fed into one end of the mill and product taken from the other.

Successful pilot plant operation showed that the bench-scale results could be duplicated on a larger scale and on a continuous or semicontinuous basis. Furthermore, it was demonstrated that the materials could be handled satisfactorily in the tube mill. Plugging and other difficulties were overcome.

Finally, an economic comparison of the process with an equivalent, standard, normal superphosphate process indicated that the quick-curing process was favored. Fixed capital, production cost and working capital were estimated to be less than for a conventional, normal superphosphate process. The estimated return on investment for a conventional plant was 3.8 per cent while the equivalent quick-curing plant gave an estimated 5.6 per cent.

INTRODUCTION

An important product of the reaction between sulfuric acid and phosphate rock is normal superphosphate. From the standpoint of tonnage produced, this fertilizer material ranks first. As a result, many studies relative to its production have been made. The present work was concerned with (1) the effect of grinding during the reaction between sulfuric acid and phosphate rock and (2) the optimum drying conditions for the reaction mixture.

Some of the variables considered in these studies were grinding temperature, grinding time, drying temperature, final moisture content, acidulation ratio and acid concentration.

The Process

Reactions

It has been reported (27, 28) that the main constituent of phosphate rock is fluorapatite. The principle products of the action of sulfuric acid on fluorapatite are monocalcium phosphate and calcium sulfate. The over-all reaction assumed to occur is frequently written

$$Ca_{10}F_2(PO_4)_6 + 6H_2SO_4 + 3H_2O \longrightarrow 3Ca(H_2PO_4)_2 \cdot H_2O + 6CaSO_4 + CaF_2 \qquad (1)$$

In practice, however, a part of the CaF_2 reacts with additional acid to produce hydrogen fluoride. Between 20 and 35 per cent of the fluorine in the rock is evolved.

Commercial normal superphosphate differs from the so-called double

or triple superphosphate in that phosphoric acid rather than sulfuric acid is used in the acidulation. In triple superphosphate the important fertilizer compound is also monocalcium phosphate but calcium sulfate is absent in the product. As a result the total phosphate content of triple superphosphate is about three times that of normal superphosphate.

In addition to the reaction indicated by Equation 1, two side reactions occur as a result of the liberated hydrogen fluoride acting upon the silica present in the rock:

$$4HF + SiO_2 \longrightarrow SiF_4 + H_2O \qquad (2)$$

$$3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6 \qquad (3)$$

Recent evidence indicates that the over-all reaction, Equation 1, takes place in three steps (23).

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 \longrightarrow 6H_3PO_4 + 10CaSO_4 + 2HF \qquad (4)$$

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF \qquad (5)$$

$$Ca(H_2PO_4)_2 + H_2O \longrightarrow Ca(H_2PO_4)_2 \cdot H_2O \qquad (6)$$

Nunn and Dee (22) described this sequence of reactions in the following manner:

> While free sulfuric acid is still present a little monocalcium phosphate is formed but the principle reaction is the formation of free phosphoric acid. With the disappearance of sulfuric acid (which with the rock of the usual fineness of grinding and acid concentrations of 70% H_2SO_4 takes place in 30 to 40 minutes) formation of free phosphoric acid ceases. This free acid now forms 40 to 50% of the total P_2O_5 and further interaction is between this and previously unchanged rock, mainly to form mono-calcium phosphate.

The hydration of monocalcium phosphate, Equation 6, has been indicated (16, 28) to account for the setting-up or hardening of normal superphosphate.

The calcium sulfate present does not hydrate under the usual acidulation conditions. However, the hemihydrate and dihydrate of calcium sulfate are found in the product of acidulation with unusually dilute acid. Drying the product seems to minimize sulfate hydration even when dilute acid has been used.

Additional side reactions are known to occur as a result of impurities in the rock, such as:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \qquad (7)$$

$$Fe_2O_3 \cdot 3H_2O + 4H_3PO_4 \longrightarrow 2H_3Fe(PO_4)_2 + 6H_2O \qquad (8)$$

The number of pounds of pure sulfuric acid used per pound of P_2O_5 in the rock is called the acidulation ratio. It may be seen from Equation 1 that on a mole basis the acid required for the over-all reaction is 2 moles of sulfuric acid for each mole of equivalent P_2O_5 in the rock. In practice 2.6 moles of acid are used per mole of P_2O_5 to allow for the reaction between calcium fluoride and impurities with the sulfuric acid. On a weight basis this amounts to an acidulation ratio of 1.8 pounds of acid per pound of P_2O_5 in the rock. Various investigators have studied the effect of acidulation ratio on the reaction (6, 9, 17, 22, 26). They have reported that acidulation beyond a ratio of 1.8 tends to produce a product containing excessive free acid. On the other hand, underacidulation tends to produce dicalcium phosphate and incomplete reactions.

Factors affecting the reactions

It is commonly known that heat will increase the rate of reaction between acid and phosphate rock. Less common is the knowledge of the

effect heat has upon the products of the reaction.

Schlaeger (25) found that upon heating monocalcium phosphate at 212°F. it began to lose its water of hydration. In order to crystallize anhydrous monocalcium phosphate from a solution, a temperature of at least 284°F. was found necessary to prevent formation of the monohydrate. When, however, monocalcium phosphate monohydrate was heated for 5 to 20 hours at 284°F., it became coated with a glassy shell containing dicalcium phosphate. When the monocalcium phosphate was heated for 1 1/4 hours at 446°F. the product contained 7 per cent calcium acid pyrophosphate. Dragunov (7) reported that heating monocalcium phosphate to a temperature as low as 302°F. resulted in the formation of some pyrophosphate. The pyrophosphate is a rather insoluble form of phosphate and not suitable as a fertilizer. Laboratory investigations by the Tennessee Valley Authority (3) with concentrated superphosphate indicated that heating the superphosphate a few hours at 392°F. resulted in only a slight loss in phosphate solubility, while heating at temperatures above 572°F. resulted in a marked decrease in solubility.

For many years superphosphate producers were adverse to drying superphosphate because of the possibility of reversion of the soluble monocalcium phosphate to an insoluble form (10, 23). Some of the confusion lay in the distinction between water solubility and neutral ammonium citrate solubility since dicalcium phosphate, one of the products of drying, is insoluble in water but soluble in neutral ammonium citrate.

Most states now recognize the solubility of phosphates in neutral

ammonium citrate as a criterion of availability[1].

A large proportion of the superphosphate produced is presently used for mixed fertilizer goods in which much of the nitrogen is added by ammonia. Ammoniation of monocalcium phosphate produces dicalcium phosphate according to the following equation:

$$Ca(H_2PO_4)_2 + NH_3 \longrightarrow CaHPO_4 + NH_4H_2PO_4 \qquad (9)$$

If dicalcium phosphate is already present in the superphosphate, less ammonia will be absorbed at equilibrium. It would, therefore, be desirable to prevent overheating of the superphosphate in any drying operation to reduce the formation of appreciable amounts of dicalcium phosphate or the pyrophosphate.

Acid concentration also effects the rate of reaction (15, 18, 22), the initial reaction rate increasing as more dilute acid is employed. Under normal conditions of acidulation, 70 per cent sulfuric acid appears to give the best results (22). Use of higher acid concentrations results in poor mixing while the calcium sulfate formed tends to coat the particles (15). On the other hand, use of too dilute acid results in a product with a high moisture content and poor physical characteristics. The reaction is slow or incomplete with dilute acid because of the resulting low temperatures.

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[1]The term availability, used synonymously with conversion, refers to the per cent of the total P_2O_5 which is soluble in neutral ammonium citrate solution. This is official expressed as

$$100 \ \frac{\text{total } P_2O_5 - \text{citrate insoluble } P_2O_5}{\text{total } P_2O_5}$$

Acid temperature is of some importance. With cold acid the reaction is sluggish. With very hot acid the mixture of acid and rock thickens too readily (23). Acid temperatures of 100 to 150°F. are generally used (16).

The effect of grinding the rock before acidulation has been shown to be beneficial (18, 22, 23). However, in the size range of 21 to 93 per cent minus 100 mesh, the effect of the fineness of the grind is very small. Extremely fine grinding, however, does increase the rate of reaction (22). It has been postulated that coating of the rock particles with calcium sulfate is a controlling factor.

Previous Work

Ordinary superphosphate processes

The usual procedure for making normal superphosphate is quite simple: The required amounts of acid and rock are mixed and the reaction mixture is retained in some kind of closure a sufficient length of time for it to set up. The resulting porous solid is then broken up and transferred to piles for curing. About 30 days are usually allowed for the chemical reactions to go essentially to completion. The most notable changes during this curing period are the reduction in the free acid and moisture content. The change in P_2O_5 availability with time for a commercial pile (28) and a small laboratory batch are shown in Figure 1. The differences in P_2O_5 availability are largely the result of lower temperatures in the laboratory batch. The usual free acid and moisture contents of commercial superphosphate are about 3 and 5 per cent

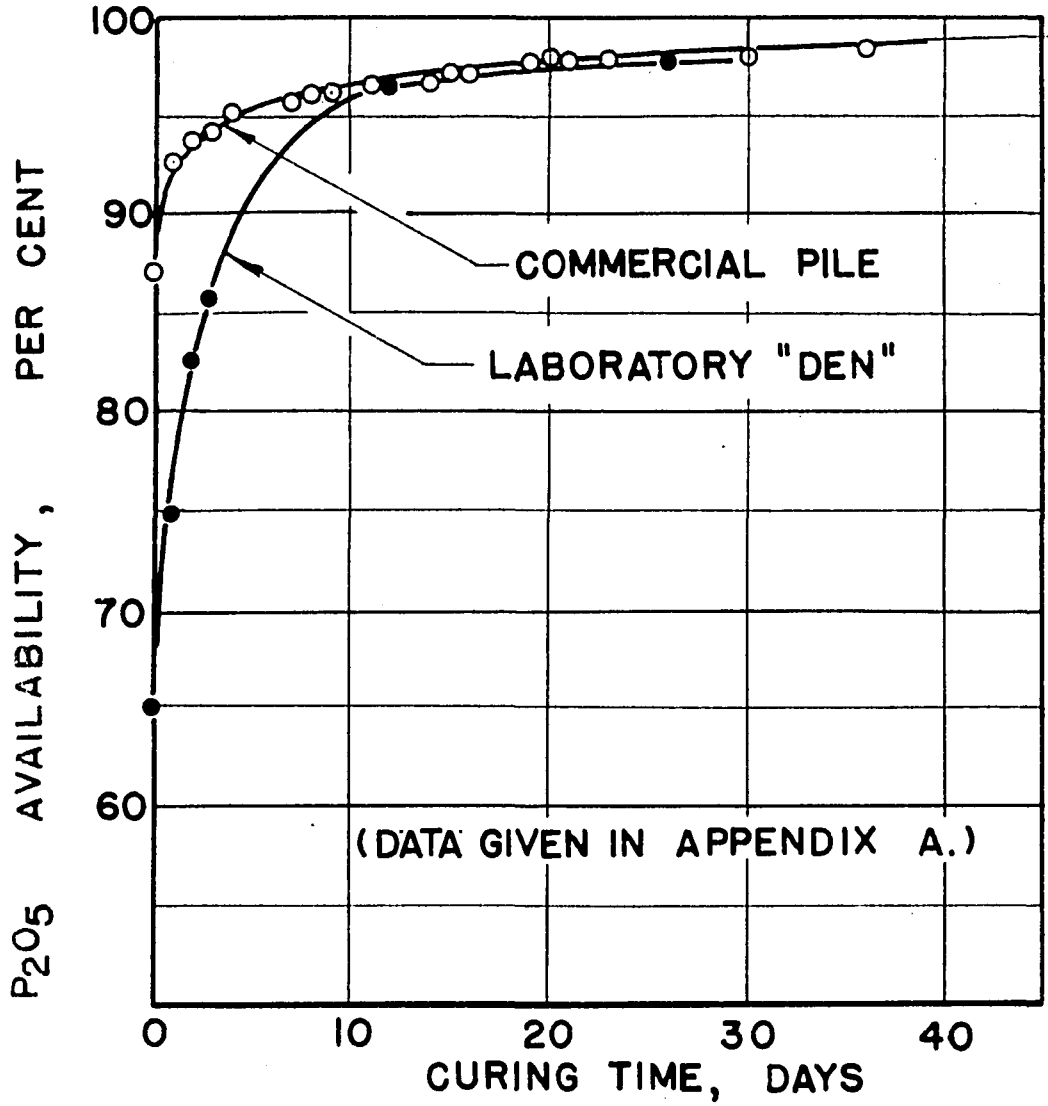


FIGURE 1. CHANGE IN AVAILABILITY WITH TIME FOR COMMERCIAL AND LABORATORY BATCHES OF NORMAL SUPERPHOSPHATE

respectively.

The closure in which the acid and rock is retained after mixing is quite varied. The oldest is a cement bin, called a den. The material is removed from this bin with a mechanical shovel. Later developments include the mechanization of the den to reduce the amount of handling required. One of the most noteworthy innovations was that of the Sturdevant den (23, 27). The Sturdevant den is really a self-propelled flat car with removable sides. The floor of the flat car serves as the floor of the den. The wall at the rear of the den is stationary while the other three walls are removable. A supporting structure around the car provides a roof for the den chamber and also supports the mixer.

A short time after the den is filled to the required height, the front and sides are removed and the solid superphosphate is disintegrated by a revolving cutter. The cutter removes the superphosphate in slices about 1/8 inch thick. At the same time, the fanning action of the blades assists in the removal of gases and steam.

Continuous processes

Several processes have been proposed in which the mixing, hold-up, and disintegration are carried out continuously. For large scale production a continuous process can result in considerable saving of manpower.

The Broadfield process is one of the best known of the continuous processes (23, 27). In this process the acid and rock are metered continuously and mixed in a pug mill having a residence time of 2 or 3 minutes. The mixed material is discharged into a den consisting of a moving, endless conveyor with two similar conveyors forming the side walls.

Siems (27) introduced a modification in which the side walls are stationary. The bottom conveyor carries the block toward a revolving cutter on an endless chain. The disintegrated superphosphate is then conveyed to storage for curing.

In the Sackett process (6, 27) fluidized rock dust and an acid spray are continuously injected into a mixing chamber. The resulting slurry falls to the bottom and is agitated by a mixer. The material is discharged onto a continuous conveyor which has a hold-up of approximately one hour. The superphosphate is disintegrated by a cutter and conveyed to storage for curing. This process is currently being used at Indianapolis, Indiana and Prairie du Chien, Wisconsin.

Quick-curing processes

A quick-curing process is one in which the curing period has been reduced or eliminated entirely. Bridger (3) suggested the following advantages of a quick-curing process:

1. The product could be shipped directly, thus reducing the storage space required and the working capital tied up in the inventory.
2. The opportunities for producing a granular superphosphate would be greater.
3. Operating conditions could be chosen with more flexibility for attaining maximum conversion.
4. Uncertainty of production rates would be eliminated because the final product would be produced in a matter of hours rather than about four weeks which are required in the storage-curing process.

An approach to quick-curing is achieved in the Davison process (35) using concentrated sulfuric acid (98 per cent) to produce a superphosphate of low fluorine content. When the acid and rock are mixed, conversion is about 75 per cent. After mixing, the material is heated at temperatures from 250 to 500°F. for about an hour to further fluorine removal. The material is then ground and fed into a rotary granulator where 14 to 18 parts by weight of water are added to increase conversion and produce a granular product. Conversion is then about 91.5 per cent. After ten days to two weeks curing, the conversion is approximately 92.5 per cent.

A quick-curing process was developed at Iowa State College (5, 8, 14) in which dilute acid, 50 to 65 per cent, was used and a product ready for immediate shipping was produced. In this process the acidulated mixture was dumped into a Sturdevant type den where solidification occurred. The mixture was disintegrated and moved by a belt conveyor to a Roto-Louvre dryer where the product was dried at temperatures below 275°F. Conversion amounted to about 93 per cent in the final product.

In 1953 a process was announced in Japan (20) in which the reaction between sulfuric acid and rock was promoted by passing an alternating electric current through the mixture for 2 1/2 hours. A conversion of about 96 per cent was obtained as a result of this treatment. However, an exceptionally high acidulation ratio was used to achieve the quick-curing effect.

In January of 1957 the Tennessee Valley Authority announced a process (13) for quick curing normal superphosphate. They used ultra-finely ground phosphate rock with an excess of dilute acid.

The economics of the last two processes are of dubious merit because

of the amount of acid used. This may not, however, preclude their use in mixed goods.

BENCH-SCALE WORK

Materials and Equipment

The Florida pebble phosphate rock used for this study was obtained from the Davison Chemical Corporation plant at Perry, Iowa. Although the rock was transported from the plant and stored in covered 55-gallon steel drums, sufficient moisture was present or adsorbed to cause agglomeration. In order for the feeding mechanism to work smoothly it was necessary to have the rock of uniform size. The rock was therefore passed through a gyratory crusher and rolls to break up the lumps. Little, if any, actual grinding took place.

Moisture and free acid analyses were carried out according to the procedures of the Association of Official Agricultural Chemists (2). The colorimetric procedure of Bridger, Boylan and Markey (4) for phosphate was used in the determination of P_2O_5. Analyses of samples of the phosphate rock were found to agree substantially with those of Drobot (8) who originally purchased and analyzed the rock. Table 1 gives the chemical analysis of the rock as determined by Drobot (8).

Screen analyses were made with a Tyler Ro-Tap. These analyses differ somewhat from those of Drobot. Apparently considerable agglomeration had taken place. The size distribution of the rock before grinding is shown in Table 2.

Table 1. Chemical composition of Florida pebble phosphate rock (dry basis)

Component	Weight per cent	Component	Weight per cent
CaO	47.8	SO_3[a]	0.2
MgO	0.4	Fe_2O_3	1.05
F	4.6	Al_2O_3	1.35
P_2O_5	33.4	SiO_2	9.07
B.P.L.[b]	72.8	Moisture	0.51

[a]Not determined by Drobot

[b]Represents bone phosphate of lime or equivalent per cent of $Ca_3(PO_4)_2$

Table 2. Screen analysis of the Florida pebble phosphate rock

Screen mesh	Weight per cent of sample
+65	7.1
- 65 +100	15.1
-100 +150	7.5
-150 +200	27.2
-200	43.1

Concentrated sulfuric acid was diluted to about 72 per cent for use in the laboratory work. The exact concentration was then determined by titration. The density was evaluated with an accurate hydrometer.

A ball mill was selected to carry out the grinding for several reasons: (1) simplicity of construction, (2) ease of heating, and (3) adaptability to fine grinding. The use of a ball mill for phosphate rock grinding has been previously demonstrated (21, 23).

All bench-scale grinding was accomplished in the laboratory, one quart, stainless steel ball mill shown in Figure 2. The mill contained 4.5 pounds of 0.75 inch stainless steel balls. The mill cover was equipped with a vent tube in a rotating joint, as shown in Figures 3 and 4, to permit refluxing of the vapor or drying to take place at atmospheric pressure.

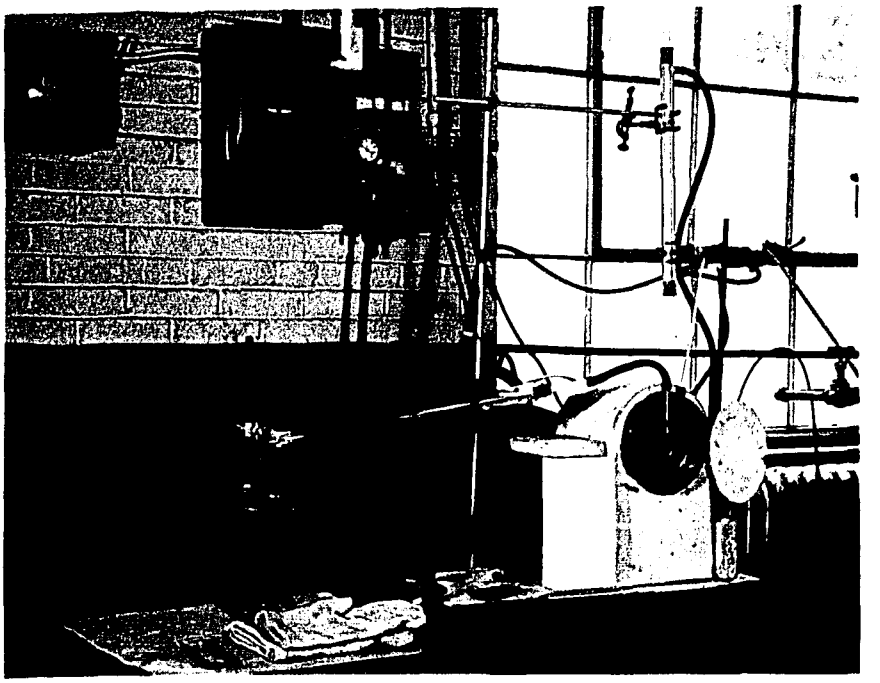
The ball mill itself was enclosed in a chamber which could be heated indirectly as shown by Figure 4. This heating shell was constructed of 18 gage galvanized iron and provision was made to measure the temperatures of the gas within the mill chamber.

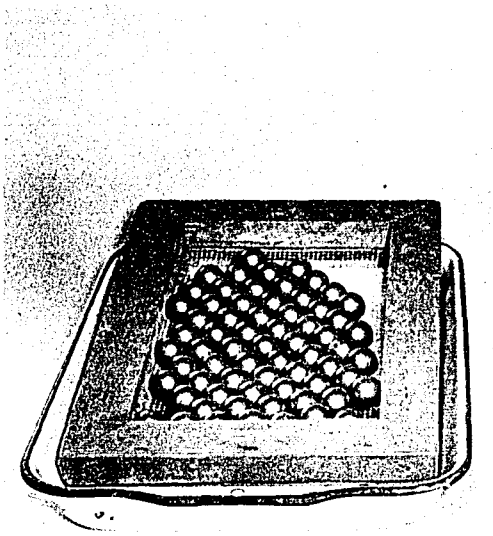
The mill was equipped with two condensers. A vertical condenser was used to reflux any escaping vapors when drying was not desired and an inclined condenser, shown connected in Figure 2, was used to condense the vapors coming from the mill during the drying operation. Measurement of the amount of condensate gave a good indication of the progress of drying.

A 10 mesh screen was used to separate the hot dried product from the balls after the final drying step.

Figure 2. Assembled laboratory ball mill and heating unit

Figure 3. Disassembled laboratory ball mill with balls and screen for recovering product





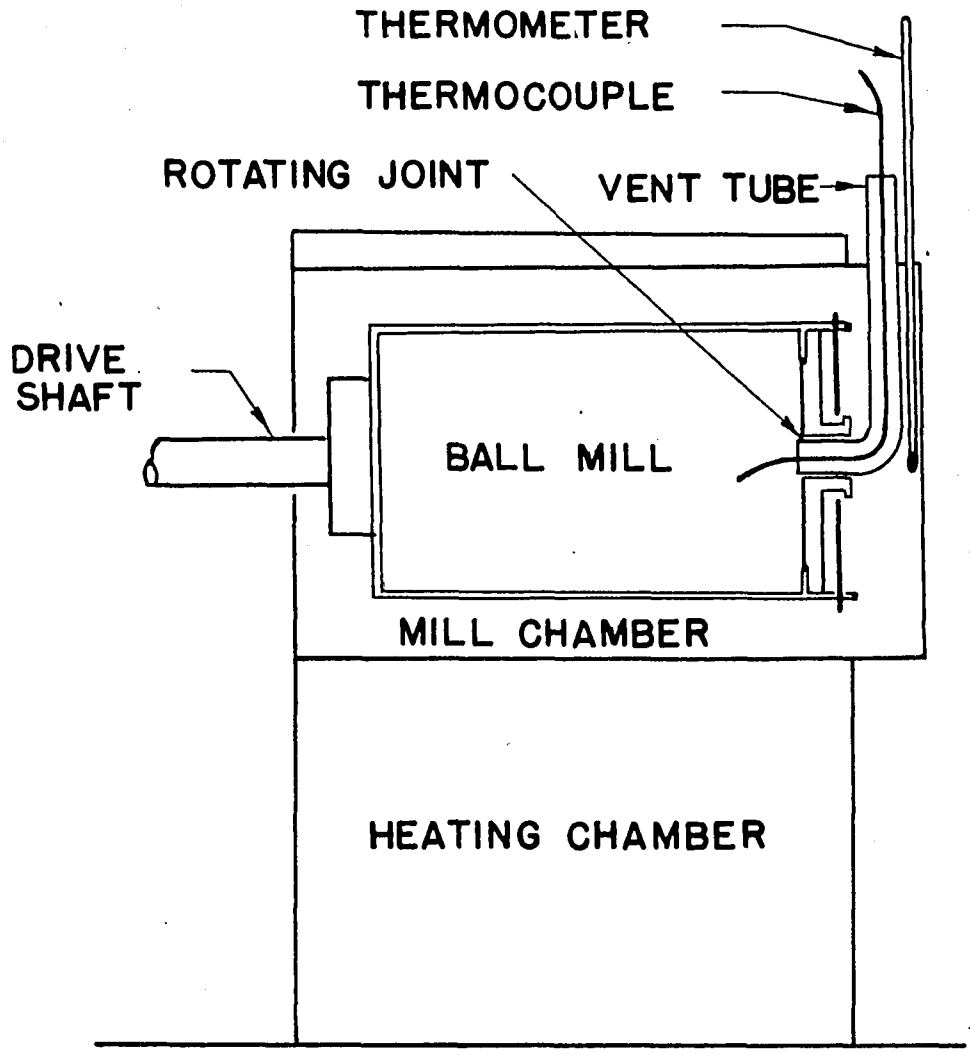


FIGURE 4. CROSS SECTION OF BALL MILL AND HEATING UNIT

Procedure

In all cases the desired quantities of 72 per cent sulfuric acid and rock were first mixed in a glass beaker. Much of the hydrogen fluoride was evolved at this point. The mixture was then emptied into the mill and the last traces of rock and acid were washed from the beaker with the required amount of water to give the proper acid strength.

After the mill was assembled, grinding was started and the reflux condenser attached. Heated grinding was accomplished by maintaining the mill chamber temperature between 110 and 115°C. Actual product temperature at this point was about 103°C., measured by means of a thermocouple inserted through the vent tube into the mill. Because it could not stand the abuse within the mill the thermocouple was used intermittently. Care had to be taken to prevent the rotating joint from becoming plugged and causing pressure within the mill.

When the grinding action with reflux had continued for the desired length of time, drying was started. The reflux condenser was removed, the inclined condenser connected and the heat input was increased to maintain the required mill chamber drying temperature. It was discovered in earlier runs that a white, crystalline precipitate formed in the condenser tube at a product moisture content of about 3 or 4 per cent. The precipitate was silicic acid which resulted from the evolution of silicon tetrafluoride in the side reactions Equations 2 and 3, and was observed by Siems to occur at a product temperatures between 102 and 113°C. (28). This precipitate formation was used as a criterion for stopping the drying operation in many of the runs.

At the end of the drying step the product was removed from the mill and immediately sealed in a sample bottle for analysis. The balls and mill were cleaned for the next run by replacing the balls in the mill, adding water, running the mill for about 10 minutes and finally rinsing with clean water.

Analyses of the product samples were carried out according to the same procedure as for the rock samples. These analyses were made as soon as possible after completion of a run. Where the moisture content was high or samples were taken "wet", the analyses were started immediately. Analysis of samples with less than 5 per cent moisture were frequently allowed to stand overnight. Determination of conversion as a function of time for these samples showed that the change in conversion was negligible in this period. This was also suggested by Bridger and Kapusta (5).

Results and Evaluation of Results

Quick-cured normal superphosphate was made in the laboratory ball mill in batches containing 50 and 100 grams of rock. The variables studies were grinding temperature, grinding time, drying temperature, acidulation ratio and acid concentration. The results of these studies are given in Table 3.

In order to ascertain more completely what occurs upon acidulation of phosphate rock, a microscopic examination of the rock before and after acidulation was made. The production of a large amount of fines is the primary effect. Figures 5 and 6 are photomicrographs showing this effect.

Table 3. Laboratory ball mill data

Run no.	Weight of rock gm.	Acidul. ratio	Acid conc., per cent	Prelim. grind	Drying temp. °C.	Product analysis, per cent					
						Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Moist.	Free acid
54A	50	1.45	39.1	hot[a]	125	21.6	4.2	17.4	80.6	2.53	-
56A	50	1.45	39.1	hot	125	22.5	4.2	18.3	81.5	2.33	-
61-I	100	1.80	39.1	cold[b]	150	20.5	1.0	19.5	95.1	3.34	2.28
61-II	100	1.80	39.1	cold	150	20.0	0.7	19.3	96.5	2.91	1.56
61-III	100	1.80	39.1	cold	150	20.3	1.1	19.2	94.6	2.67	1.56
62-I	100	1.80	39.1	cold	125	19.8	0.6	19.2	97.0	5.02	1.11
62-II	100	1.80	39.1	cold	125	19.7	0.6	19.1	97.0	4.08	1.94
63-II	100	1.80	39.1	cold	125	20.4	0.8	19.6	96.0	3.39	1.91
64-I	100	1.80	39.1	cold	150	21.7	1.2	20.5	95.5	3.33	3.28
64-II	100	1.80	39.1	cold	150	21.2	1.4	19.8	93.5	3.90	2.14
65	100	1.80	39.1	cold	125	21.2	1.0	20.2	95.5	3.25	1.14
69	100	1.80	39.1	cold	135	20.3	0.8	19.5	95.9	3.78	0.87
70	100	1.80	39.1	hot	135	20.6	0.8	19.8	96.1	3.98	0.60
71	100	1.80	39.1	hot	125	20.9	0.7	20.2	96.6	4.66	2.34
72	100	1.80	44.6	cold	125	21.8	0.7	21.1	96.9	2.60	3.42
73	100	1.80	39.1	hot	125	21.6	1.1	20.5	94.9	4.90	0.74
74	100	1.58	37.4	hot	125	22.1	2.6	19.5	88.1	2.66	2.08
75	100	1.80	39.1	hot	150	20.3	1.0	19.3	95.0	3.53	2.36
76	100	1.80	39.1	hot	125	20.7	0.6	20.1	97.1	3.43	0.56
77	100	1.80	55.5	cold	125	22.5	1.2	21.3	94.6	3.46	1.81

[a]Mill chamber temperature was 115°C.

[b]About room temperature

Table 3. (Continued)

Run no.	Weight of rock gm.	Acidul. ratio	Acid conc., per cent	Prelim. grind	Drying temp. °C.	Product analysis, per cent					
						Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Moist.	Free acid
78	100	1.80	72.2	cold	125	22.6	4.3	18.3	80.9	2.56	2.62
79	100	1.80	39.1	hot	135	20.7	0.8	19.9	96.0	2.78	2.55
80-I	100	1.80	39.1	hot	150	20.8	0.7	20.1	96.6	3.07	1.88
81	100	1.80	39.1	cold	135	20.7	1.0	19.7	95.2	3.40	1.21
82	100	1.58	37.4	hot	125	21.6	2.1	19.5	90.3	3.17	0.13
87	100	1.80	39.1	cold	165	20.4	0.6	19.8	97.1	3.46	0.94
89	100	1.80	55.5	none	125	20.3	0.5	19.8	97.5	5.81	1.79
90	100	1.80	39.1	cold	135	21.7	0.9	20.8	95.8	2.73	2.51
91	100	1.80	55.5	none	135	25.5	1.5	24.0	94.2	4.06	3.24
92-I	300	1.80	39.1	- [c]	- [d]	14.2	3.6	10.6	74.6	-	9.05
92-II	300	1.80	39.1	- [e]	135	21.0	1.1	19.9	94.7	2.58	3.04
93	100	1.80	39.1	cold	185	20.6	0.5	20.1	97.6	4.69	1.67
94-I	100	1.80	61.1	cold	125	21.9	1.2	20.7	94.5	2.75	2.74
94-II	100	1.80	61.1	cold	125 [f]	21.5	0.9	20.6	95.8	3.82	2.34
96-II	100	1.80	39.1	cold	125	21.4	0.7	20.7	96.7	3.18	1.50
97	100	1.80	39.1	cold	200	19.9	0.6	19.3	97.0	4.32	2.14
104	100	1.80	39.1	cold	125	20.4	0.5	19.9	97.5	3.31	1.54
115	100	1.80	39.1	45 min.	- [d]	13.9	1.2	12.7	86.3	-	-
120	100	1.80	55.5	none	135	21.0	0.6	20.4	97.2	1.94	1.59

[c] Material mixed in Mixmaster rather than mill

[d] Analysis of wet material ground cold, no drying used

[e] Material from 92-I placed in mill for drying

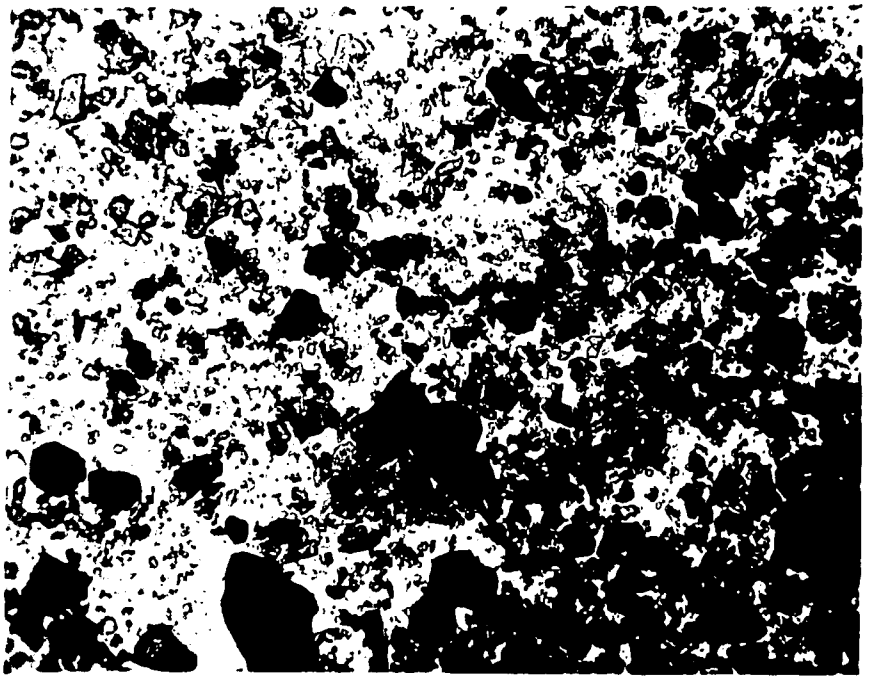
[f] Analysis of material caked on wall of mill

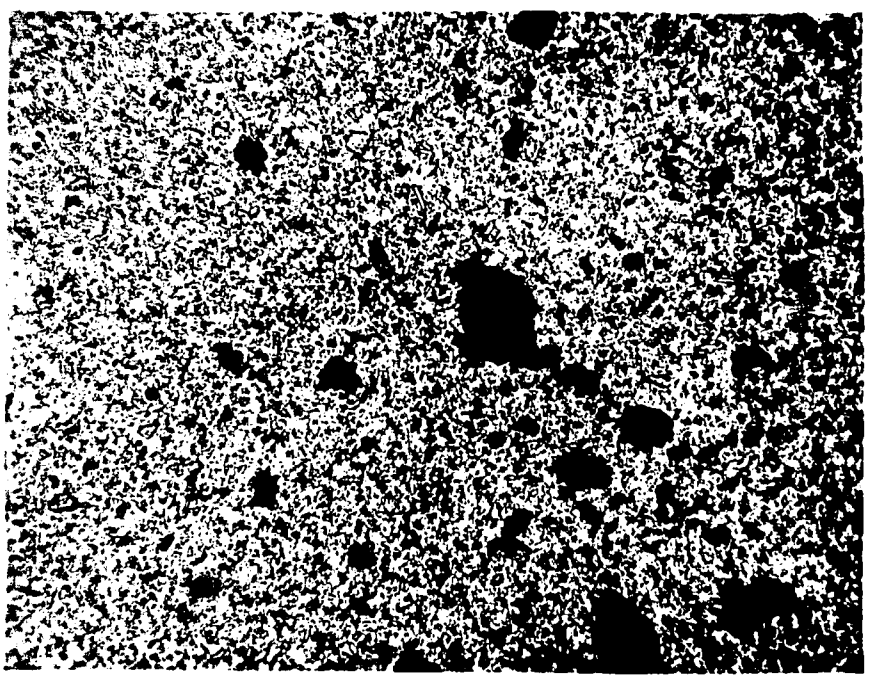
Table 3. (Continued)

Run no.	Weight of rock gm.	Acidul. ratio	Acid conc., per cent	Prelim. grind	Drying temp. °C.	Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Moist.	Free acid
121-I	100	1.80	39.1	15 min.	- [d]	13.4	2.8	11.6	86.5	-	-
121-II	100	1.80	39.1	30 min.	- [d]	19.2	2.6	16.6	86.5	-	-
121-III	100	1.80	39.1	60 min.	- [d]	13.9	2.0	11.9	85.6	-	-
122-I	100	1.80	39.1	none	- [d]	18.8	7.8	11.0	58.5	-	-
122-II	100	1.80	39.1	5 min.	- [d]	13.0	2.0	11.0	84.6	-	-
132	100	1.80	72.0	cold	125	20.6	1.5	19.1	92.8	0.54	-
134	100	1.80	72.0	cold	125	20.8	2.0	18.8	90.4	3.17	-
150	100	1.02	50.0	cold	125	25.2	10.7	14.5	57.5	2.63	1.32

Figure 5. Photomicrograph of raw phosphate rock, 100X magnification

Figure 6. Photomicrograph of freshly acidulated phosphate rock, 100X magnification





The break up of the rock on acidulation as shown in these photos should be of considerable interest for commercial production. These fines, however, do not contribute heavily to the total weight.

The effect of mill chamber drying temperature on the conversion of normal superphosphate is shown in Figures 7 and 8. The samples were preground either hot or cold for 45 minutes before starting the drying operation. These data indicate that grinding temperature has little or no effect on the final conversion of the product. The data also indicate no significant difference between pregrinding the sample with or without heating.

Actual measurements of the product temperature were made when a mill chamber drying temperature of 185°C. was used. Although the product temperature measurements were made about 5 minutes after the moisture had dropped to 3 per cent, as indicated by the precipitate formation in the condenser, the product temperature was still below 147°C. After 5 more minutes the product temperature increased another 10 degrees. This indicated that, generally, the mill chamber drying temperature had little effect on the product temperature as long as the moisture content of the product was above 3 per cent. The only effect was on the drying rate.

It may be noted that drying proceeded rapidly in the ball mill even at temperatures as low as 125°C. in the mill chamber. Recently Hatch and Regen (12) investigated drying under similar conditions with equally rapid drying rates.

No consistent correlation between final free acid and moisture content was indicated and little variation was found in the actual value of either. Free moisture content varied between 2.5 and 4.9 per cent while the free

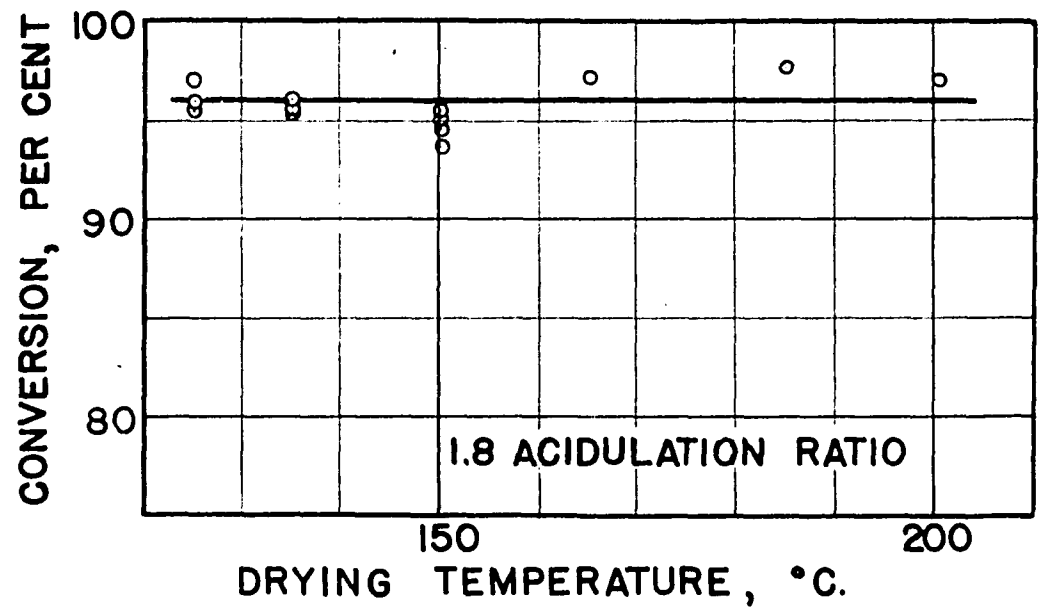


FIGURE 7. EFFECT OF DRYING TEMPERATURE ON CONVERSION, PREGROUND AT 30°C.

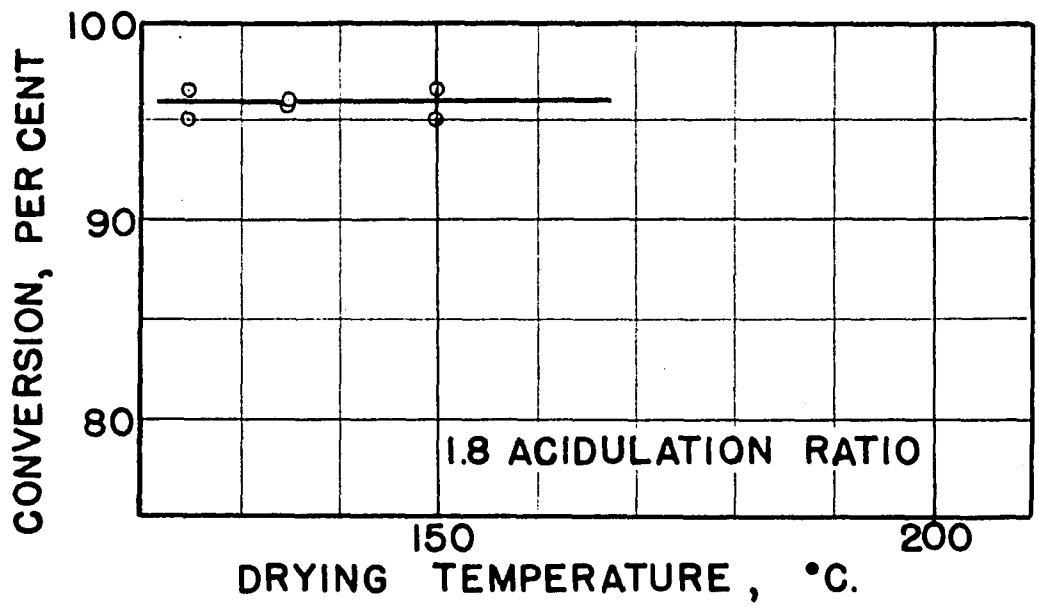


FIGURE 8. EFFECT OF DRYING TEMPERATURE ON CONVERSION, PREGROUND AT 103°C.

acid content ranged from 0.5 to 3.5 per cent. These values compare favorably with common commercial superphosphate (27).

Decrease in the acidulation ratio below the recommended 1.8 caused a rapid drop in the conversion of the product as shown in Figure 9. This same effect of acidulation ratio was noted by Bridger and Kapusta (5).

Figure 10 shows that the effect of acid concentration used in the acidulation was small as long as the acid strength was below 55 per cent. Below this concentration conversion dropped off rapidly. The data of Bridger and Kapusta for the Roto-Louvre dryer quick curing show the same effect indicating a primary effect upon conversion of the moisture content of the original mixture. It was noted that at these high acid concentrations the balls did not move freely in the mixture.

The results of runs 89, 91 and 120 in Table 3 indicate that high conversion (about 95 per cent) could be obtained if the drying were started immediately, without preliminary grinding. To check this, samples were taken "wet" from the mill during the grinding period and analyzed. In Figure 11 the effect of grinding time on the availability is shown. This indicates that long preliminary grinding is unnecessary. However, conversions higher than 86 per cent were not obtained.

The drying step does, therefore, seem to increase the conversion. This has also been noted by Meyers (19) who showed that concentrating a dilute phosphoric acid and rock mixture in a rotary dryer promoted the reaction. Several rapid-curing processes have been built in Europe (10, 23) on this basis.

To determine whether the high conversions obtained in the ball mill were the result of grinding or of good mixing or drying technique,

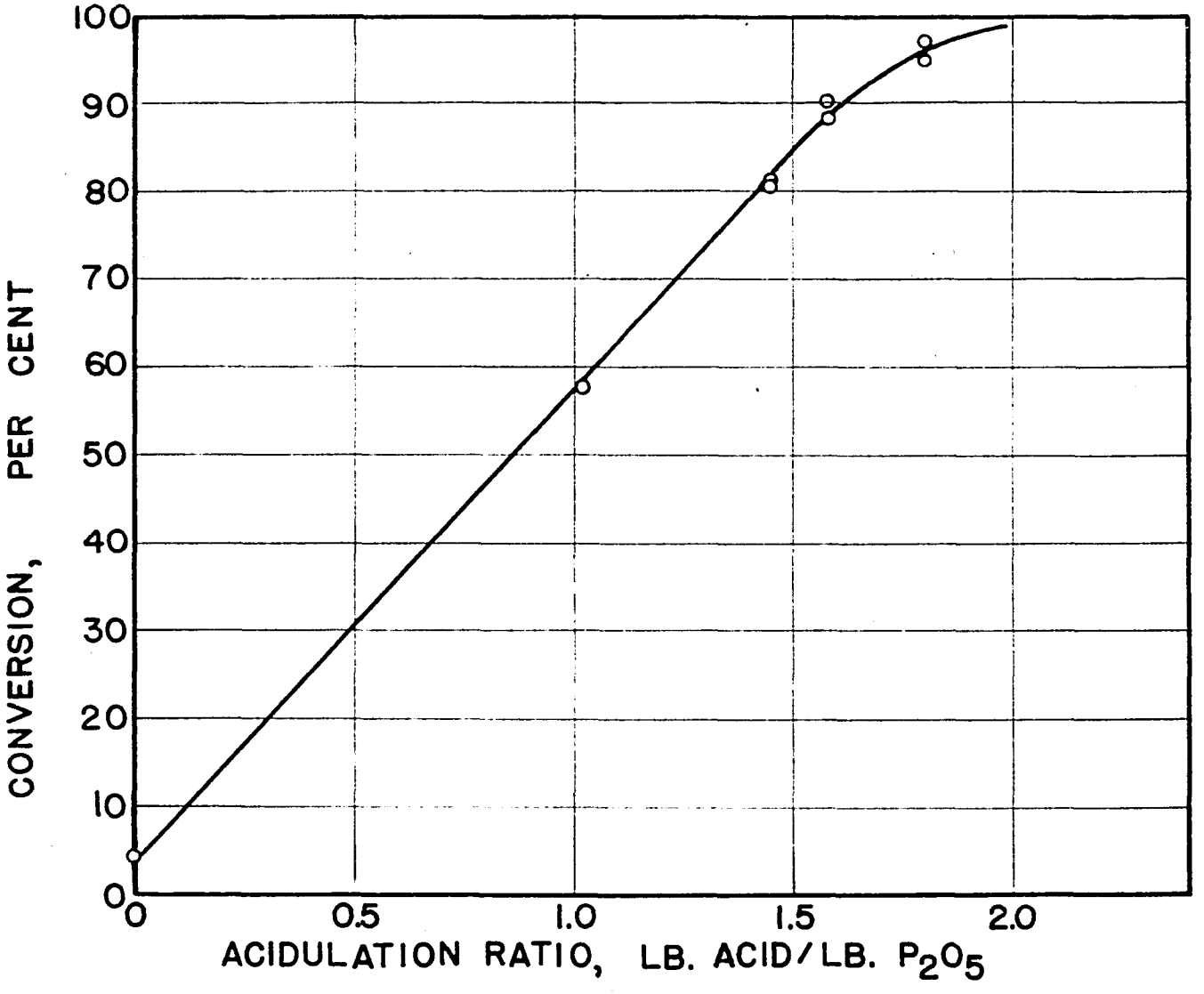


FIGURE 9. EFFECT OF ACIDULATION RATIO ON CONVERSION

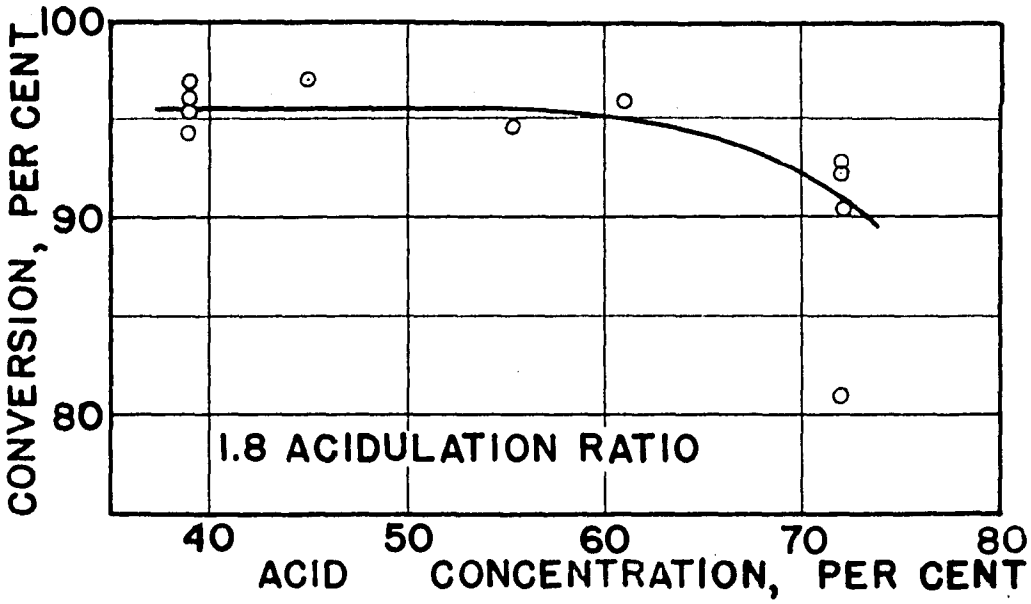


FIGURE 10. EFFECT OF ACID CONCENTRATION ON CONVERSION

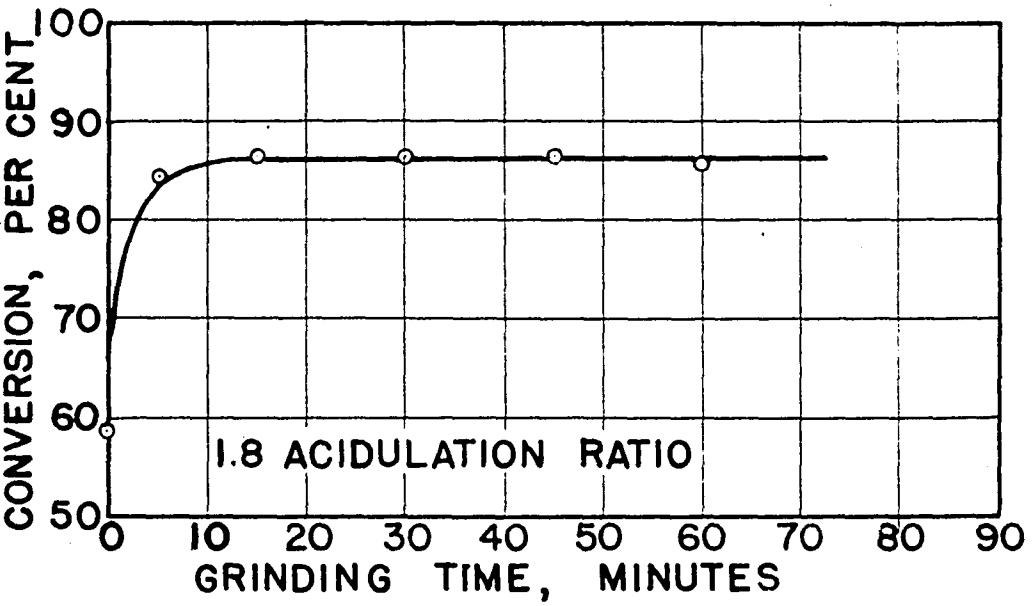


FIGURE 11. EFFECT OF GRINDING TIME IN BALL MILL ON CONVERSION

acidulations were made using a Sunbeam Mixmaster model 9 and the laboratory ball mill as a control. Analyses were made immediately after mixing (10 minutes), after 45 minutes in the Mixmaster and after 45 minutes in the ball mill. The results are given in Table 4. It is evident that the ball mill is superior. Furthermore, this process represents an improvement in conversion over the process of Bridger and Kapusta (5) in which the basis was drying technique alone.

Table 4. Comparison of conversion with and without grinding

Run	Sample	Free acid per cent	Conv. per cent
84-I	Freshly mixed rock (10 min.)	-	65.0
92-I	45 minutes in Mixmaster	9.05	74.6
76-I	45 minutes in ball mill (cold)	7.60	82.5

The results of the bench-scale work showed that a quick-curing process was possible using a laboratory ball mill. To show that the process could be adapted to a larger scale a pilot plant for production of 50 to 100 pounds per hour was constructed. It was expected that the pilot plant work would assist in solving the related problems in materials handling, grinding and heat transfer.

PILOT PLANT WORK

Materials and Equipment

The phosphate rock used in the pilot plant runs was from the same lot as that used in the bench scale work. The sulfuric acid used was 66° Baumé acid obtained from the General Chemical Division of Allied Chemical and Dye Corporation. The acid was diluted with distilled water to the desired strength.

A flow sheet for the pilot plant is given in Figure 12. The pilot plant consisted essentially of a continuous, heated, lined tube mill with provision for feeding acid and rock and removing product. The acid entered the mill from a rotameter while the rock was fed with a vibrating feeder. The acid and rock were mixed, ground and dried in the mill where the action of the balls and the addition of heat accelerated the reaction. The product was discharged from the opposite end of the mill in a powdered or granular form. The mill was heated by means of an air heater connected to a shell around the tube mill. A portion of the used hot air was recycled while the remainder was blown from the building. The vapors from drying and the fluorides produced by the side reactions were removed at the feed end of the mill. They were scrubbed to remove the fluorides and separated in a cyclone to remove water droplets. The remaining gas was exhausted from the building. A photograph of the pilot plant is shown in Figure 13. Figure 14 shows the product end of the mill.

The tube mill itself was made from a 6 foot length of standard 12

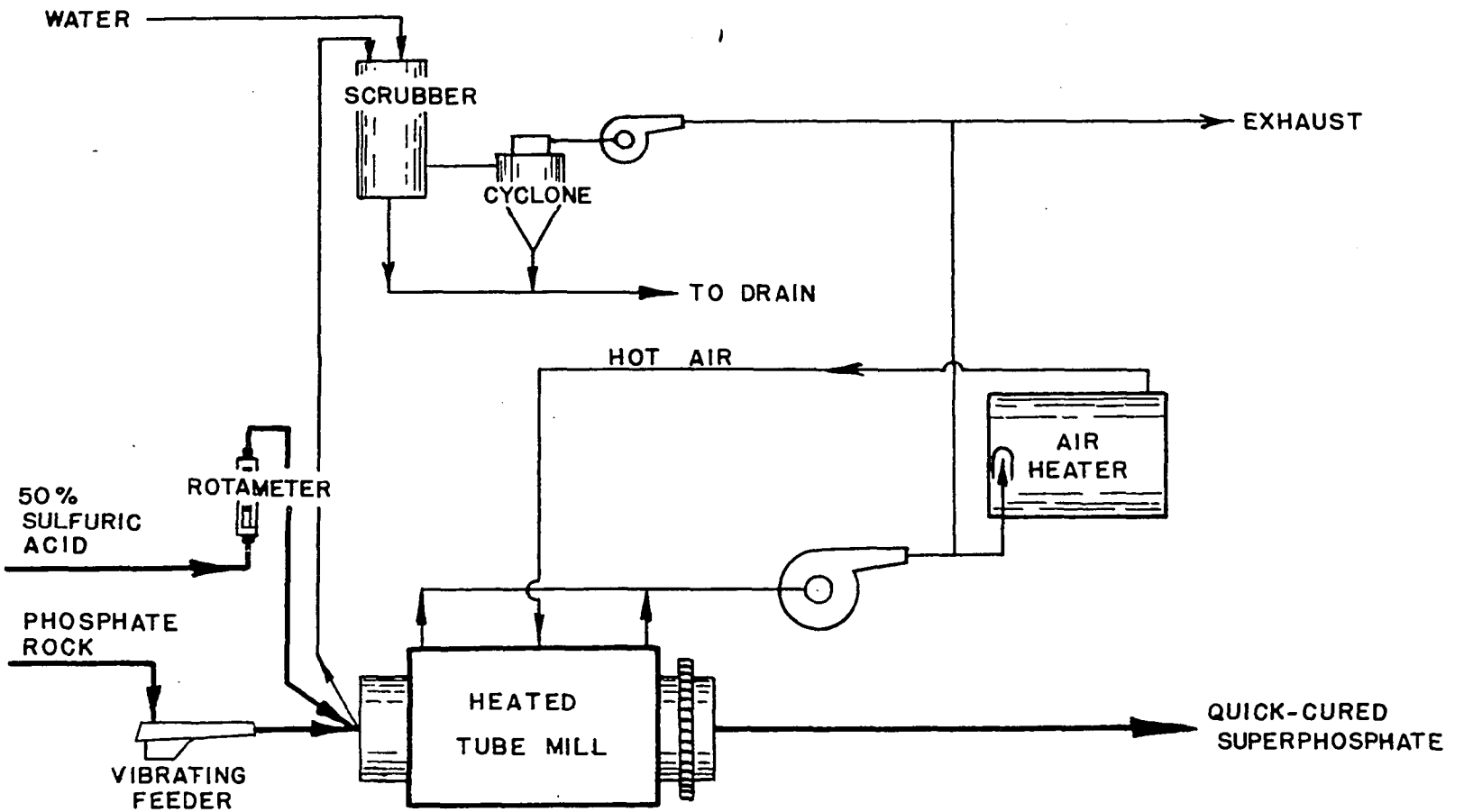
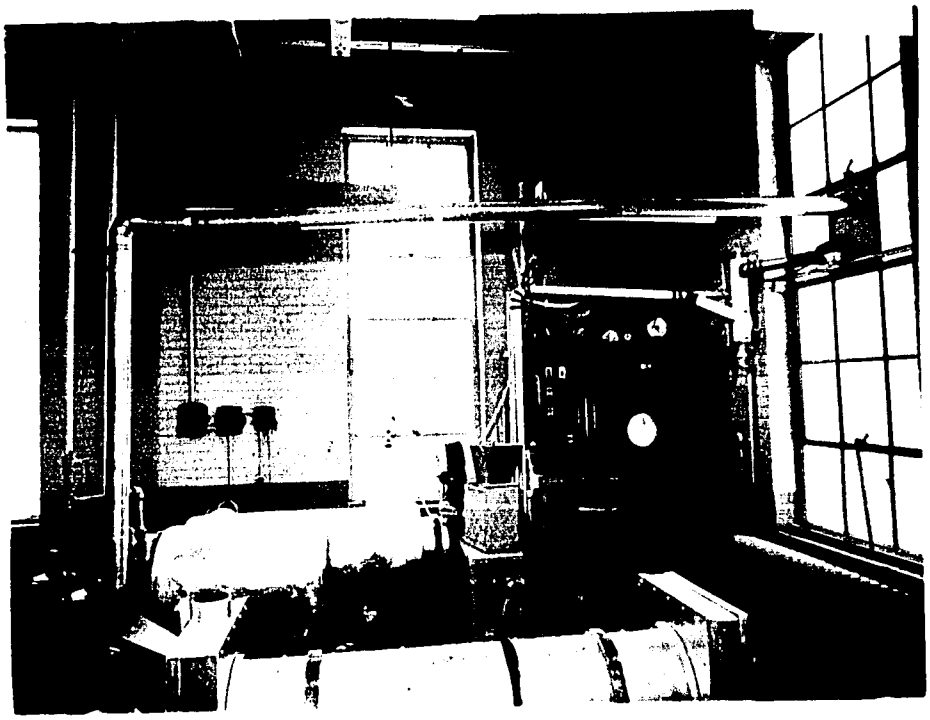
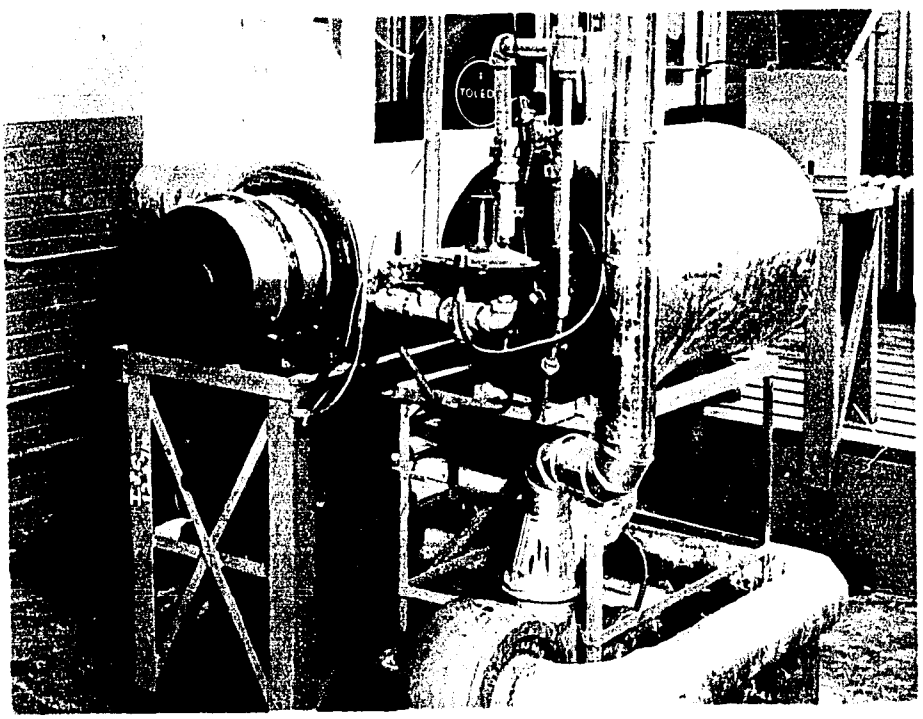


FIGURE 12. FLOW SHEET OF A QUICK-CURING PILOT PLANT FOR NORMAL SUPERPHOSPHATE

Figure 13. Over-all view of quick-cured normal superphosphate pilot plant

Figure 14. View of discharge end of tube mill

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inch pipe. The two tires upon which the mill rolled were made from short sections of 14 inch pipe machined to fit snugly over the 12 inch pipe. These tires rested on cast iron rollers mounted on ball bearing pillow blocks. A detailed description of the equipment is given in Table 5.

The mill was driven by a 8:1 ratio chain drive from a Link Belt speed reducer to a large sprocket mounted on the 12 inch pipe. The speed reducer was driven through a 1:1 V-belt drive by a 1 horsepower motor. The mill speed could be varied if necessary by a change in the V-belt pulley size between the motor and speed reducer.

The mill was lined with 16 gage stainless steel, type 302. This lining was attached to the mill, after it had been rolled to fit, with four, stainless steel angle irons running the length of the mill and bolted through the shell. The angle irons acted as "baffle bars" which lifted the balls and allowed them to impact against the acid-rock mixture.

Stainless steel ends were attached to the mill with socket head screws. Tapped holes for the screws were provided in the wall of the shell. The feed end contained a rotating seal enclosing the feed and exhaust ducts.

The stationary heating jacket consisted of a 54 inch section of 18 inch outside diameter, 1/4 inch wall pipe. This length allowed space at each end of the heating jacket for the tire and drive sprocket mountings outside the jacket. Hot air entered the jacket tangentially at the center and was removed tangentially at both ends. The relative temperatures at either end were adjusted by controlling the hot air flow with dampers in the return air ducts. The hot air return ducts were joined and connected to a blower. From the blower a portion of the air was recycled through the

Table 5. Description of purchased pilot plant equipment

Item	Description
Acid mixer	Redmond model 3593, 115V., 60 cycle, 0.5 amp., series 3U, type L, 1/160 hp.
Bearings	Link Belt, self aligning ball bearings, 1 in. shaft, No. P216
Blower, mill	Buffalo Forge Co., series U670, 12 in. impeller, 3600 r.p.m.
Blower, exhaust	Ilg fan, 1/100 hp., 110V., 60 cycle
Burner	Hauck, model PAC-L-779
Controller	Brown, model 602P1E-20-74, series 453555, bulb 74437-600, 115V., 60 cycle motor, chart 12525
Control motor	Minneapolis-Honeywell Grad-U-Motor, model M0 900C28X1
Feed drive	Palomeyers mixer motor, model 7609-C, 1/18 hp., with rheostat, 110V., 60 cycle
Gas valve	Minneapolis-Honeywell magnetic gas valve, type V835A2DJ8, 3/4 in., 4 oz., 24V., 60 cycle, 0.75 amp.
Gas pressure regulator	Fisher Converter, type 730C-1, outlet 3-8 in., water column, orifice 1/2 in.
Humidity recorder	Brown recorder, model 6882-609, series 403342, chart 1565, 0-100% H., 0-100°F.
Motor, blower	Marble Card Electric Co., induction motor, No. 14317, 2 hp., 3 phase, 220V., 60 cycle, 5.5 amp.,
Motor, mill	Westinghouse induction motor, 1 hp., 3 phase, 220-440V., 60 cycle, series 5606, S# 1778265A
Pump	Eastern Industries pump, B1, type 100, assem. 60189, series C3D1343, metal M.
Rotameter	Fisher & Porter Flowrator, V67-403211 (plastic float, lead loaded)
Speed reducer	Link Belt worm gear drive, model WB30-56, ratio 5 5/6:1
Sprockets	Link Belt, A.S.A. No. 50, 72 tooth sprocket (machined to fit 12 in. pipe)
Temperature indicator	Brown indicating controller, model 105C2P-20-55 series 237358, switch 25 amp. at 100V.
Transformer	General Electric, cat. 2333, 4-24V. secondary, 110V., 60 cycle primary, 50 watt
Vibratory feeder	Syntron, type FC0, style 1283, 110V., 60 cycle, 0.7 amp., series E 5C322331

burner while the rest of the air was exhausted from the building.

Heat was supplied by a Hauck combination oil-gas burner equipped for natural gas. A combustion chamber was made from a 2 foot section of 12 inch pipe surrounded by a 20 inch concentric shell of 16 gage sheet metal through which the recycle portion of the gases passed. The recycle stream entered tangentially at the burner end. The hot burner gases and recycle stream were mixed at the discharge end of the combustion chamber.

The burner setting was regulated by a Minneapolis-Honeywell Grad-U-Motor, a pneumatically operated mechanism. The air pressure to operate the motor was received from a Brown controller and recorder with a 1 to 10 per cent proportional band. The output pressure to the motor depended both on the temperature indicated by the sensing element and the temperature at which the controller was set. The sensing element consisted of a liquid filled bulb. This was inserted in the duct for the air leaving the heating jacket of the mill at the product end. Therefore, the basis for control of the burner was this exit gas temperature.

The gas was led to the burner through a magnetic gas valve. This valve could be operated by opening and closing the electrical circuit to the magnetic valve. As a safety precaution, the temperature of the hot gases coming from the burner was measured by means of a thermocouple and indicated on a Brown indicating controller. The controller was so connected that a sudden drop in temperature, such as might be experienced from a flame failure, would be immediately indicated by a light and buzzer. This was accomplished by setting the set point of the controller to about 10 degrees below the operating temperature of the burner.

The controls mentioned previously along with all of the other necessary

controls were conveniently located on a panel at the feed end of the mill. The panel is shown in Figure 15. Manometers for measuring the pressure of the burner air, the burner itself, the inlet end of the mill and both of the hot air return ducts, were likewise placed on the panel.

The rock was fed by a Syntron vibrating feeder into a metal funnel connected by a 1 inch stainless steel tube to the mill. The tube contained a 5/8 inch auger driven by a laboratory mixer to provide a continuous flow of solids into the mill. The acid was fed directly into the mill from a rotameter. Both the acid and rock entered the mill through the stationary portion of the rotating seal. Because the rock feeder calibration was affected by humidity, a humidity and temperature recorder was provided on the panel.

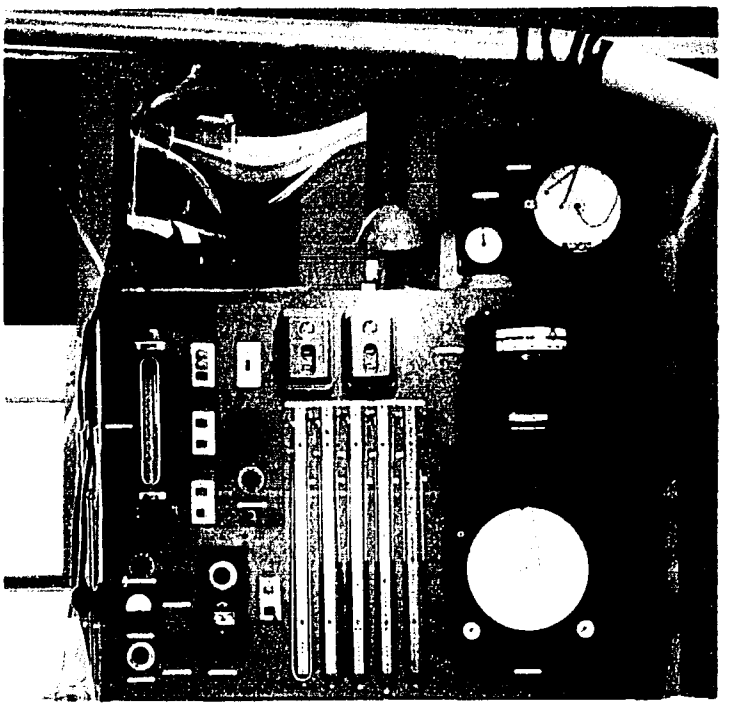
The water vapor and fluorides were exhausted from the feed end of the mill with a small blower. The gases were scrubbed with water to remove the fluorides, exhausted through a cyclone to remove water droplets and discharged to the atmosphere by an Ilg blower.

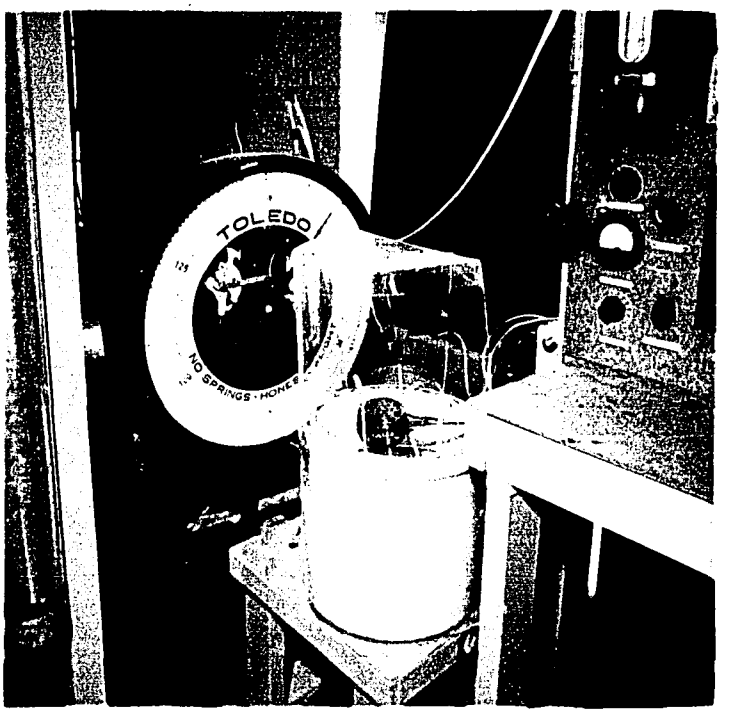
The sulfuric acid, approximately 93 per cent, was diluted to 50 per cent before use. This was accomplished in batches of about 35 pounds by mixing the water and acid in a 5 gallon porcelain crock equipped with 30 feet of 1/4 inch, tygon coated, copper tubing for cooling. A laboratory mixer was used to agitate the solution for improved heat transfer. The dilution equipment is shown in Figure 16.

From a pipe connected to the bottom of the mixing vessel the cooled, mixed acid was pumped to a glass storage receiver above the control panel. This allowed the acid to be fed to the mill by gravity. Both the mixing vessel and the acid storage bottle were shielded with plexiglass in case

Figure 15. Control panel for quick-cured normal superphosphate pilot plant

Figure 16. Equipment used to dilute and cool sulfuric acid




TOLEDO
NO SPRINGS · NONE

of accidental breakage or other acid spillage.

Procedure

Before starting pilot plant operation it was necessary to heat the mill to near the operating temperature. This was accomplished by lighting the burner and setting the automatic controller to the desired temperature. With a 10 per cent proportional band used on the controller, the burner remained fully on until the temperature was within 20°F. of the set point. Approximately 1 1/2 hours were required to reach a temperature of about 450°F. at the product end of the mill.

When the operating temperature had been reached, the rock and acid feed were started at a predetermined rate. The feeding of the rock was generally started first (1) to prevent excess corrosion of the mill in the presence of free, hot sulfuric acid and (2) to prevent accumulation of moisture in rock feeder tube which tended to clog the feeder.

The first four runs were made to develop an operating technique and to find weak points in the pilot plant construction. After each of these runs extensive changes and repairs were made in preparation for a continuous, steady state run. Feeding, therefore, was intermittent in those runs and even in the early part of the final run. Irregular operation of the mill was experienced, because of partial plugging of the exhaust vent at the feed end. This caused accumulation of moisture and prevented drying of the product. Once this was remedied steady state could be readily reached.

As criteria for steady state operation uniform feed and product rates

were used. Thus, a material balance in and out was attained.

From time to time it was necessary to dilute additional acid in the acid mixer and transfer it to the storage tank. Although the water and acid were weighed, the large tare weight of the container and accessories plus the electrical and cooling water connections made the weighings less sensitive than desirable. Therefore, the concentration of the diluted acid was measured by means of an accurate hydrometer. The dilute acid was cooled to approximately 80°F. before it was pumped to storage.

Samples were taken of the product from the mill by holding a sample bottle at the mill outlet. During steady state runs samples were taken every half hour.

Proper shutting down of the mill at the end of a run was a simple but important procedure. First the acid and rock feed were stopped and the burner shut off. The reflux blower was allowed to run, however, since the mill and heater were still hot. A strong stream of water was then introduced into the feed end of the mill. The mill was allowed to revolve until the effluent from the mill was clear. This assured that no partly reacted phosphate would remain in the mill to contaminate the following run and that all of the balls were free and clean. The mill was stopped at this point to drain the remaining water. A plug in the lower end of the mill was removed for draining. The blowers were then turned off.

Results and Evaluation of Results

Because the first four runs with the pilot plant were made for the purpose of evaluating operating technique and finding mechanical defects,

little data were collected for those runs. However, the following changes were made which affected the subsequent pilot plant operation: (1) After the first run the rock and acid feeding method was changed to that previously described. During the first run both the acid and rock were introduced through the same (glass) funnel containing a mixer. The funnel tube plugged frequently. (2) During the second run higher hot air temperatures were employed and found to be desirable. (3) A more thorough method for washing was employed after the third run. Abnormally high SO_3 analyses in the product from the later part of the second run were found. This was also found on the third run. It was surmised that the washing technique at the end of a run was responsible for leaching the soluble phosphate but leaving the insoluble sulfate in the mill. (4) A better scrubbing unit and cyclone were installed to alleviate plugging of the exhaust blower by silicic acid. (5) The rotary seal was modified and replaced on the fourth run.

The data for the preliminary and the steady state runs are given in Table 6. The first digit of the sample number indicates the run number. The data for the last part of run 2 and run 3 have been omitted since poor washing technique at the end of the previous runs resulted in faulty SO_3 analyses.

Difficulty was experienced with the variation of the vibrating feeder calibration with air humidity. To evaluate the changing rock flow rates, analyses were made for SO_3 in the product. Since the only significant source of SO_3 was the sulfuric acid and the rock was the only source of P_2O_5, the acidulation ratio could be evaluated.

Conversion of all samples taken during good operation of the pilot

Table 6. Quick-curing pilot plant data

Sample no.	Rock feed rate (lb./min.)	Outlet air temp. °F.	Inlet air temp. °F.	Product analysis, per cent							Acidul. ratio
				Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Moist.	Free acid	SO_3	
1-01	0.50	350	620	19.4	2.3	17.1	88.2	11.0	5.0	27.6	1.71
1-02	0.50	350	620	18.5	0.7	17.8	96.2	8.2	8.5	32.6	2.13
2-01	0.30	400	770	20.7	0.0	20.7	100.0	1.66	-	36.1	2.13
2-02	0.30	400	768	22.4	0.8	21.6	96.5	0.37	2.46	38.1	1.95
4-01	0.50	450	825	25.2	10.4	14.8	58.7	2.72	1.76	21.3	1.00
4-02	0.50	450	800	24.0	6.6	17.4	72.5	3.74	1.07	23.3	1.06
4-03	0.50	450	800	25.1	10.9	14.2	56.7	2.94	1.20	20.2	0.95
4-04	0.50	450	800	23.8	7.0	16.8	70.6	3.60	0.91	23.2	1.17
4-05	0.50	450	800	23.1	4.1	19.0	82.2	4.09	1.13	25.1	1.31
5-01	0.35	450	850+	22.3	4.7	17.6	79.0	4.03	2.07	26.0	1.41
5-02	0.30	450	850+	20.0	2.0	18.0	90.0	4.78	2.25	29.9	1.80
5-03	0.30	450	850+	20.8	3.3	17.5	84.2	3.70	3.43	29.4	1.71
5-04	0.30	450	850+	20.3	1.7	18.6	91.6	4.76	2.02	29.8	1.78
5-05	0.20	450	850+	21.5	2.7	18.8	87.5	3.86	3.31	29.5	1.66
5-06	0.20	450	850+	21.1	0.9	20.2	95.8	6.98	1.89	29.2	1.67
5-07	0.20	450	850+	25.1	9.0	16.1	64.2	3.79	0.47	21.0	1.00
5-08	0.20	450	850+	27.2	14.2	13.0	47.8	2.67	0.76	18.3	0.80
5-09	0.20	450	850+	27.0	15.1	11.9	48.0	2.66	0.36	16.0	0.70
5-10	0.20	450	850+	27.7	16.5	11.2	40.5	2.42	0.28	14.2	0.60
5-11	0.20	450	850+	26.8	15.2	11.6	43.3	1.88	0.25	12.7	0.55
5-12	0.20[a]	450	850+	25.3	9.2	16.1	63.6	2.13	0.32	22.2	1.05

[a]Approach to steady state operation

Table 6. (Continued)

Sample no.	Rock feed rate (lb./min.)	Outlet air temp. °F.	Inlet air temp. °F.	Product analysis, per cent							Acidul. ratio
				Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Moist.	Free acid	SO_3	
5-13	0.20[a]	450	850+	28.9	16.3	12.6	43.6	1.41	0.06	16.8	0.69
5-14	0.20[a]	450	850+	27.4	15.4	12.0	43.8	1.76	0.00	16.8	0.72
5-15	0.20[a]	450	850+	27.5	15.0	12.5	45.5	0.62	0.00	15.4	0.66
5-16	0.20[a]	450	850+	27.3	13.1	14.2	52.0	0.46	0.00	21.0	0.92
5-17	0.20[a]	450	850+	26.4	10.8	15.6	59.1	2.07	0.50	22.5	1.02
5-18	0.20[a]	450	850+	25.2	11.8	13.4	53.2	5.80	0.26	17.4	0.82

plant is plotted in Figure 17 as a function of the acidulation ratio. The solid line represents the data from the bench-scale work taken from Figure 9. The data of Figure 17 clearly show that the results from the pilot plant are equivalent to those of the bench-scale ball mill. It was unfortunate that steady state results were obtained when the acidulation ratio was somewhat low (0.8-1.1). The data points near the commercial acidulation ratio of 1.8 occurred during intermittent feeding.

The most important aspect of the pilot plant work, not shown in the data, was that the sticky normal superphosphate mixture could be handled adequately on a continuous basis.

It was noted that at a product moisture content of approximately 5 per cent, a granular product was obtained. At lower moisture contents the product was a fine powder.

The method of feeding, although adequate for a pilot plant, could conceivably be changed for commercial scale production to a funnel type mixer having no moving parts (3).

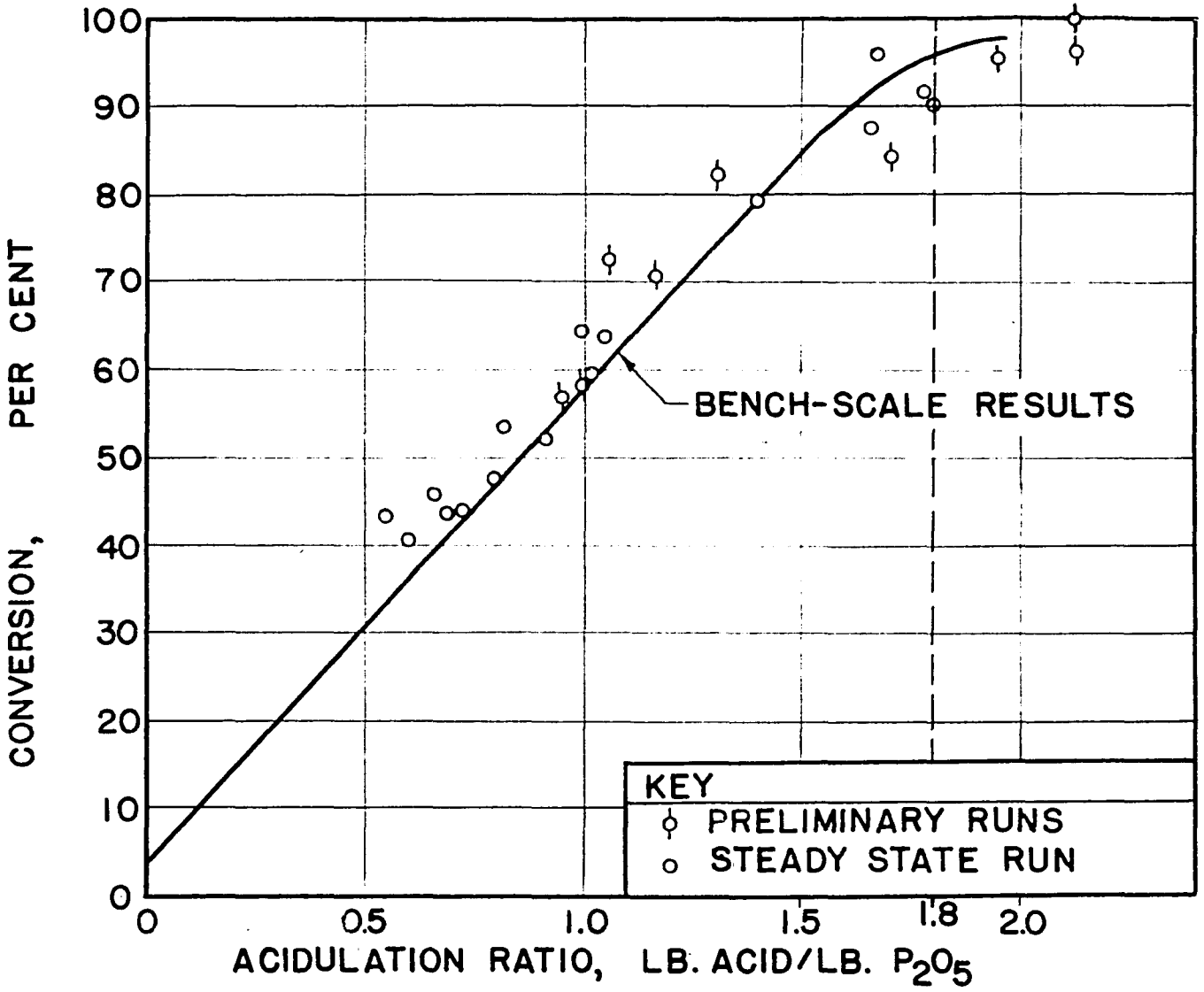


FIGURE 17. ACIDULATION RATIO AND CONVERSION OF PRODUCT FROM PILOT PLANT RUNS

ECONOMIC EVALUATION OF THE PROCESS

Proposed Process

A proposed layout for a 480 ton per day, quick-cured, normal superphosphate plant is shown in Figure 18. In the proposed layout the rock and acid are brought in by railroad cars. The rock is conveyed to a storage pile of two weeks capacity and the acid is pumped to a tank holding 10 days supply. The rock is moved by conveyor from the storage pile to overhead hoppers which discharge into each of the five tube mills. The acid and water for dilution are pumped to the mills and automatically metered in proportion to the rock. Since it has been reported that a ball or tube mill is capable of handling the grinding of phosphate rock (21, 23), no preliminary rock grinding equipment has been provided. In addition, the break-up of the rock on addition of acid could be used to advantage.

The product from the tube mills is moved by belt conveyor to an automatic bagging machine. Storage facilities for the bagged product for two weeks are provided.

An exhaust system for the mills is provided with a scrubber to remove the fluorides. The mills are heated by oil burners for each unit. The oil may likewise be brought in by railroad car. A supply of oil for 10 days to two weeks is kept on hand.

The size of the tube mills used was selected on the basis of the heat transfer area required for removal of the moisture. This size turned out to be many times the capacity of the mill so that grinding should be more

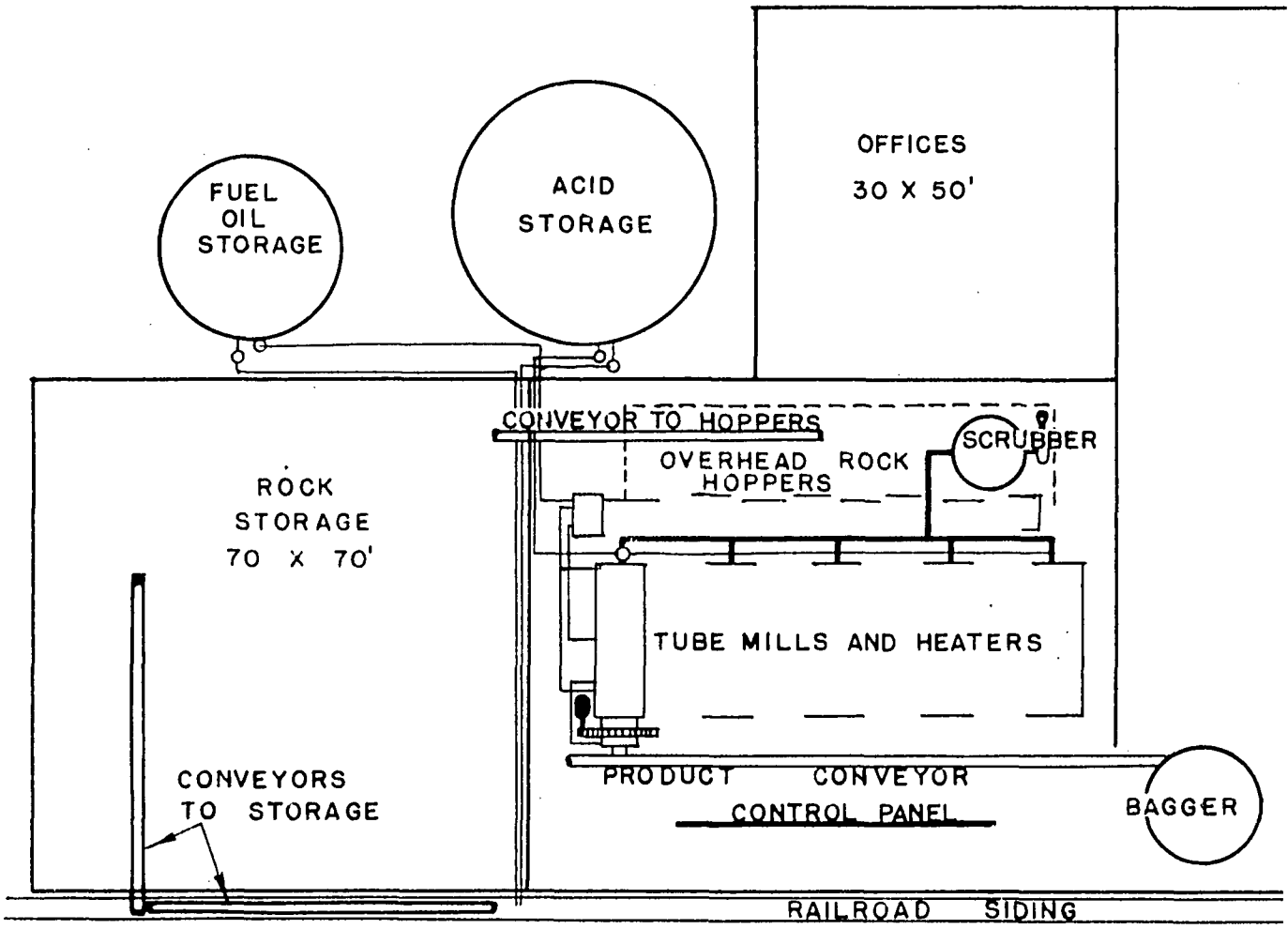
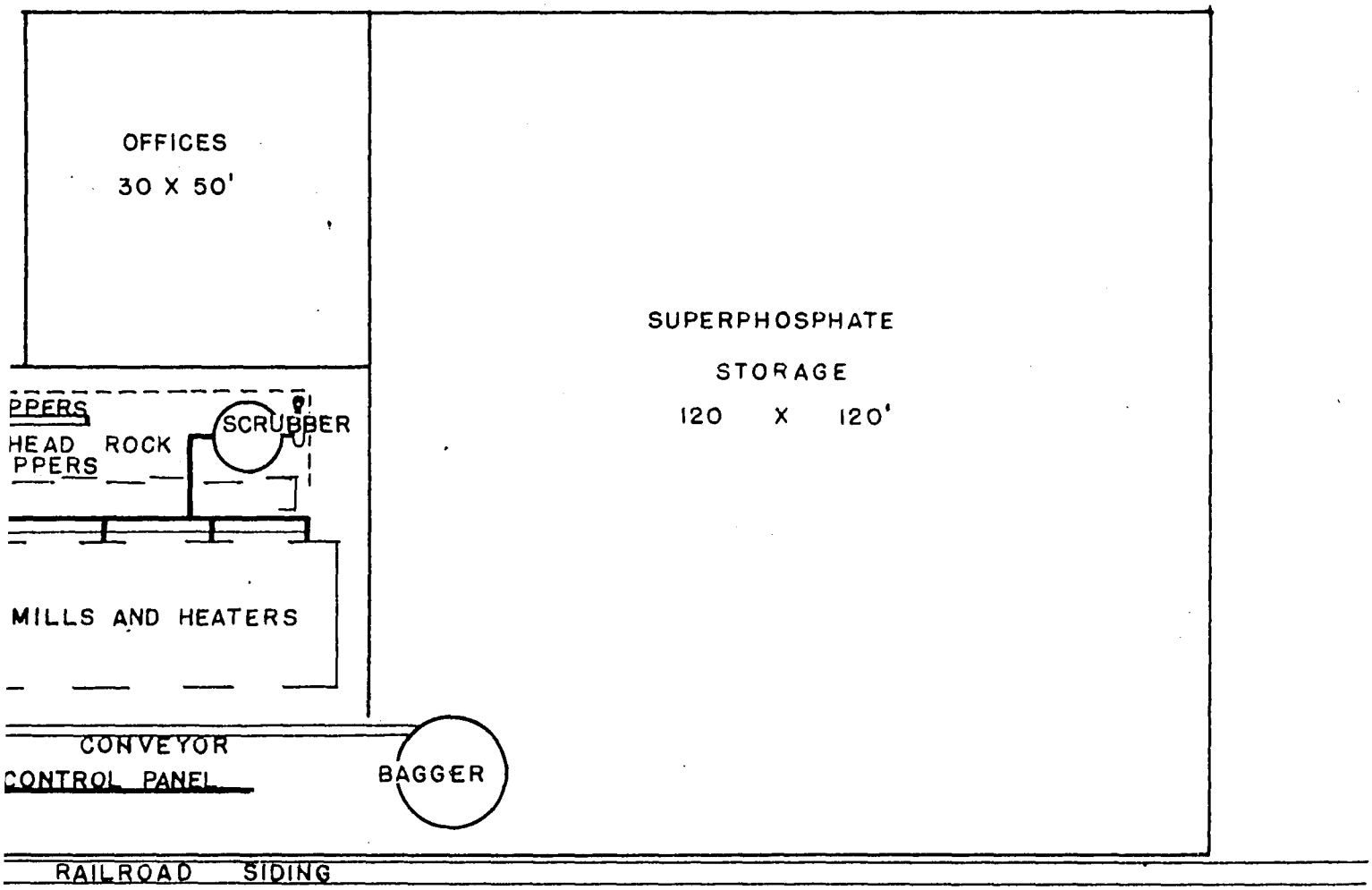


FIGURE 18. GENERAL LAYOUT OF PROPOSED QUICK-CURE



)F PROPOSED QUICK-CURED SUPERPHOSPHATE PLANT

than adequate. Some of the assumptions used in the sizing of the tube mill were:

1. The heating gases would be between 600 and 1200°F.
2. The over-all heat transfer coefficient through the mill would be 8 B.t.u./(hr.)(°F.)(ft.)^2.
3. The mill would have a stainless steel liner.
4. The heat of reaction, 105,000 B.t.u. per pound mole, would be conserved.
5. The heat from the inefficiency of grinding would not be considered.

Economic Evaluation

An estimate of the total fixed capital cost for a conventional normal superphosphate plant and for the proposed quick-curing plant is presented in Table 7. Although the total cost for the two processes is about the same, individual items in the cost estimate vary greatly. Since the batch normal superphosphate plant requires storage facilities for curing for 30 days, the handling and storage equipment for this plant is the biggest item. For the quick-curing process the grinding equipment which includes the stainless steel lined tube mills is the biggest item. Although $50,000 is listed for both processes for bagging equipment, the author who compiled the costs for the batch process (12) included superphosphate grinding equipment in this figure.

The manufacturing costs for the two processes are compiled in Table 8. Because the quick-curing process is well adapted to automatic control,

Table 7. Fixed capital cost estimates for batch and quick-curing superphosphate plants

Basis: Product - Normal superphosphate, 20 per cent available P_2O_5
Capacity - 120,000 short tons/year
Location - Ames, Iowa

(Based on December, 1956 costs)

Item	Installed cost, dollars[a] Batch	Quick-cure
Land and railroad siding	18,500	18,500
Process building	91,500	87,900
Materials handling and storage facilities	400,000	233,100
Major grinding equipment	60,000	243,700
Acid mixing and dilution equipment and dens	65,000	-
Heating equipment	-	15,100
Instrumentation and controls	-	20,500
Bagging equipment	50,000[b]	50,000
Contingencies, 20%	137,000	133,800
Total installed equipment	822,000	802,600
+ insurance and taxes, 2%	16,400	16,100
+ contractor profit, 10%	83,800	81,900
+ construction overhead, 15%	138,300	135,100
Total fixed capital investment	1,060,500	1,035,700

[a]The equipment costs for the batch process are taken from reference (11). Comparable costs for the quick-cure process, as well as the burden items for both processes, have been estimated from references (1, 29, 32).

[b]Includes superphosphate grinding equipment

Table 8. Production cost estimates for batch and quick-cured normal superphosphate plants

Basis: 1 ton of normal superphosphate
20% available P_2O_5
20 tons/hour
250 days/year

Location: Ames, Iowa
Acid source: St. Louis, Mo.
Rock source: Mulberry, Fla.

Item	Unit cost	Batch		Quick-cure	
		Quantity/ton	Cost/ton	Quantity/ton	Cost/ton
Raw materials					
Acid	$35.15/T.	0.371 T.	$13.04	0.371 T.	$13.04
Rock	15.0904/T.	0.594 T.	9.45	0.594 T.	9.45
Water	0.04/T.	0.341 T.	0.01	0.341 T.	0.01
			$22.50		$22.50
Labor					
Unskilled	$ 1.60/hr.	0.150 man-hr.	$ 0.24	0.100 man-hr.	$ 0.16
Semiskilled	2.10/hr.	0.150 man-hr.	0.32	0.100 man-hr.	0.21
Skilled	2.50/hr.	0.100 man-hr.	0.25	0.050 man-hr.	0.12
Supervision	3.00/hr.	0.0167 man-hr.	0.05	0.0167 man-hr.	0.05
Reserve	20% of above		0.16		0.11
			$ 1.02		$ 0.65
Services					
Power	$ 0.02/kw.-hr.	20.83 kw.-hr.	$ 0.42	16.67 kw.-hr.	$ 0.33
Heat	0.000467/1000 B.t.u.	577,000 B.t.u.	0.00	577,000 B.t.u.	0.27
Water	0.03/1000 gal.	208 gal.	0.01	833 gal.	0.03
Maintenance including labor	20%/yr. of fixed capital		0.44		0.43
Packaging	$ 0.15/bag		3.60		3.60
Indirect costs					
Depreciation	10%/yr. of fixed capital		0.88		0.86
Taxes and insurance	3%/yr. of fixed capital		0.27		0.26
Overhead	50% of labor		0.51		0.33
Total production cost			$29.65		$29.26

considerable saving in labor is affected. Part of the saving, however, is cancelled by the cost of heat in the quick curing process.

The working capital, net profit and return on investment are compared in Table 9 for the batch and quick-curing plants. The principle advantage for the quick-curing process is in the reduction of working capital. The batch process requires curing of the product for 30 days with a resulting large inventory; the quick-curing process requires no curing.

It may be concluded from these estimates that the quick-curing process is economically favorable in comparison with the batch, normal superphosphate process.

Table 9. Comparison of estimated return on investment for batch and quick-cured superphosphate plants

Basis: Product - Normal superphosphate
20 per cent available P_2O_5
Capacity - 20 tons/hr., 250 days/yr.
Location - Ames, Iowa

Item	Batch		Quick-cure	
	Cost/ton	Amount	Cost/ton	Amount
Annual sales[a]	$32.34	$3,880,800	$32.34	$3,880,800
Manufacturing cost		3,558,000		3,511,200
Gross profit		322,800		369,600
Administration and selling cost at 3 per cent of annual sales		116,400		116,400
Net profit, before taxes		206,400		253,200
Taxes, 50 per cent		103,200		126,600
Net profit, after taxes		$ 103,200		$ 126,600
Working capital				
Raw materials inventory				
Acid, 10 days	$35.15	$ 62,500	$35.15	$ 62,500
Rock, 2 weeks	15.09	60,300	15.09	60,300
In process inventory	29.65	427,000[b]	29.26	1,500
Product inventory	29.65	199,200	29.26	199,000
Production for 30 days	29.65	427,000	29.26	421,000
Credit, 30 days	32.34	465,500	32.34	465,500
Total working capital		$1,641,500		$1,209,800
Fixed capital		$1,060,500		$1,035,700
Total fixed + working capital		$2,702,000		$2,245,500
Per cent return on investment		3.82		5.63

[a]Based on current dealer's price in Des Moines, Iowa

[b]Based on 30 days storage

CONCLUSIONS

The following conclusions may be drawn on the basis of this work on quick-curing normal superphosphate in a ball mill:

1. Normal superphosphate of commercially marketable grade can be produced without curing by ball mill grinding during acidulation and subsequent drying.
2. Both acidulation and drying may be accomplished in a single unit on a pilot plant scale.
3. Phosphorus pentoxide conversions higher than 95 per cent can be obtained on both a laboratory and pilot plant scale.
4. The pilot plant can be operated satisfactorily on an intermittent or continuous basis and at acidulation ratios of 0.7 to 1.8 pounds of acid per pound of P_2O_5 in the rock.
5. The proposed process appears to be economically favorable in comparison to the conventional process.
6. The fixed capital and manufacturing cost for the quick-curing process are slightly lower than for the conventional process while the working capital is considerably lower.

RECOMMENDATIONS

The following are recommended with regard to further operation of the pilot plant:

1. The optimum operating conditions of the plant should be determined.
2. The maximum capacity of the pilot plant should be determined.
3. The operating conditions suitable for the direct production of a granular product should be determined.

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APPENDIX A

Analyses During Curing of Laboratory and Commercial Samples

Table 10. Change in analysis of laboratory and commercial normal superphosphate during curing

Sample no.	Curing time, days	Product analysis, per cent				
		Total P_2O_5	C.I. P_2O_5	Avail. P_2O_5	Conv.	Free acid
Laboratory samples[a]						
84-I	0	19.4	6.8	12.6	65.0	
84-II	1	19.4	4.9	14.5	74.8	13.10
84-III	2	19.6	3.4	16.2	82.6	6.64
84-IV	12	19.9	0.7	19.2	96.5	2.08
84-V	26	21.8	0.5	21.3	97.8	3.14
96-I[b]	3	13.8	1.9	11.9	86.2	
Commercial pile[c]						
	0	19.60	2.51	17.09	87.1	10.97
	1	19.80	1.43	18.38	92.8	7.85
	2	19.98	1.24	18.74	93.5	8.22
	3	19.98	1.14	18.84	94.3	7.91
	4	19.90	0.95	18.95	95.2	6.49
	7	19.98	0.85	19.13	95.7	5.88
	8	19.92	0.75	19.17	96.2	5.64
	9	19.88	0.78	19.18	96.4	5.39
	11	20.12	0.70	19.42	96.5	4.90
	14	20.02	0.65	19.37	96.7	4.90
	15	20.12	0.55	19.57	97.2	4.66
	16	20.00	0.55	19.45	97.3	4.53
	19	20.10	0.45	19.65	97.7	4.41
	20	19.98	0.37	19.61	98.0	4.41
	21	20.10	0.45	19.65	97.7	4.17
	23	20.08	0.40	19.68	97.9	3.92
	30	20.32	0.37	19.95	98.2	3.43
	36	20.10	0.25	19.85	98.7	3.31

[a]Control samples cured in laboratory

[b]Small sample mixed with 39.1 per cent acid and cured for three days.

[c]Industrial samples reported by Siems (28)

APPENDIX B

Effectiveness of Grinding

Early work with the laboratory ball mill raised a question of the effectiveness of the grinding accomplished in the mill. In order to evaluate this, size determinations were made on samples before and after grinding. Samples were taken from the mill and immediately washed with distilled water to remove any free acid or dissolved materials. The mixture was filtered and rewashed and the product either screened or examined with a microscope.

Particle sizes larger than 200 mesh (74 microns) were determined by wet screening through standard Tyler screens. From the weight of material retained on each screen, a size distribution curve was determined.

Particle sizes and distributions below 200 mesh were determined by counting the number of particles in a given size range under a microscope fitted with a Bausch and Lomb microscope screw micrometer eyepiece. The eyepiece was calibrated against a micrometer graduated to 0.01 millimeters. Weight distributions for these particles were computed on the premise that the weight of each particle in a given size range was proportional to the cube of the average diameter in that size range.

The measured size distribution are given in Table 11 and plotted in Figures 19, 20 and 21. The change in size distribution caused by acidulation was slight as shown by Figure 19. The difference in distributions as shown may be attributed to experimental error. Although a large number of fine

Table 11. Screen analysis and microscope count data

Material	Tyler screen size	Size range, microns	No. count	Approx. relative weight	Weight per cent	Cumul. weight per cent
Raw phosphate rock	+65	+208			7.1	100.0
	-65	-208			15.1	92.9
	-100	-147			7.5	77.8
	-150	-104			27.2	70.3
	(200)	-75	27	512	36.0	43.1
		-37.6	28	64	4.6	7.1
		-18.8	90	8	1.9	2.5
		-9.4	288	1	0.6	0.6
Acidulated phosphate rock	+65	+208			13.5	100.0
	-65	-208			15.7	86.5
	-100	-147			17.7	70.8
	-150	-104			17.2	53.1
	-200	-74			21.7	35.9
		-38.4	45	64	11.3	14.2
		-19.2	80	8	2.3	2.9
		-9.6	146	1	0.6	0.6
Acidulated rock, grd. 15 min.		-150	1	4096	51.1	100.0
		-75.2	2	512	12.8	48.9
		-37.6	24	64	19.2	36.1
		-18.8	80	8	8.0	16.9
		-9.4	715	1	8.9	8.9
Acidulated rock, grd. 30 min.	-30	-30	1:20	3380	2.2	100.0
	-15	-15	3	729	28.7	97.8
	-10.5	-10.5	17	216	48.1	69.1
	-6.7	-6.7	15	27	18.5	21.0
	-2.8	-2.8	195	1	2.5	2.5
Acidulated rock, grd. 60 min.		-15	6	729	53.0	100.0
		-10.5	13	216	34.1	47.0
		-6.7	34	27	11.1	12.9
		-2.8	146	1	1.8	1.8
Small mill load, grd. 60 min.		-10.5	2	216	13.6	100.0
		-6.7	96	27	81.7	86.4
		-2.8	148	1	4.7	4.7

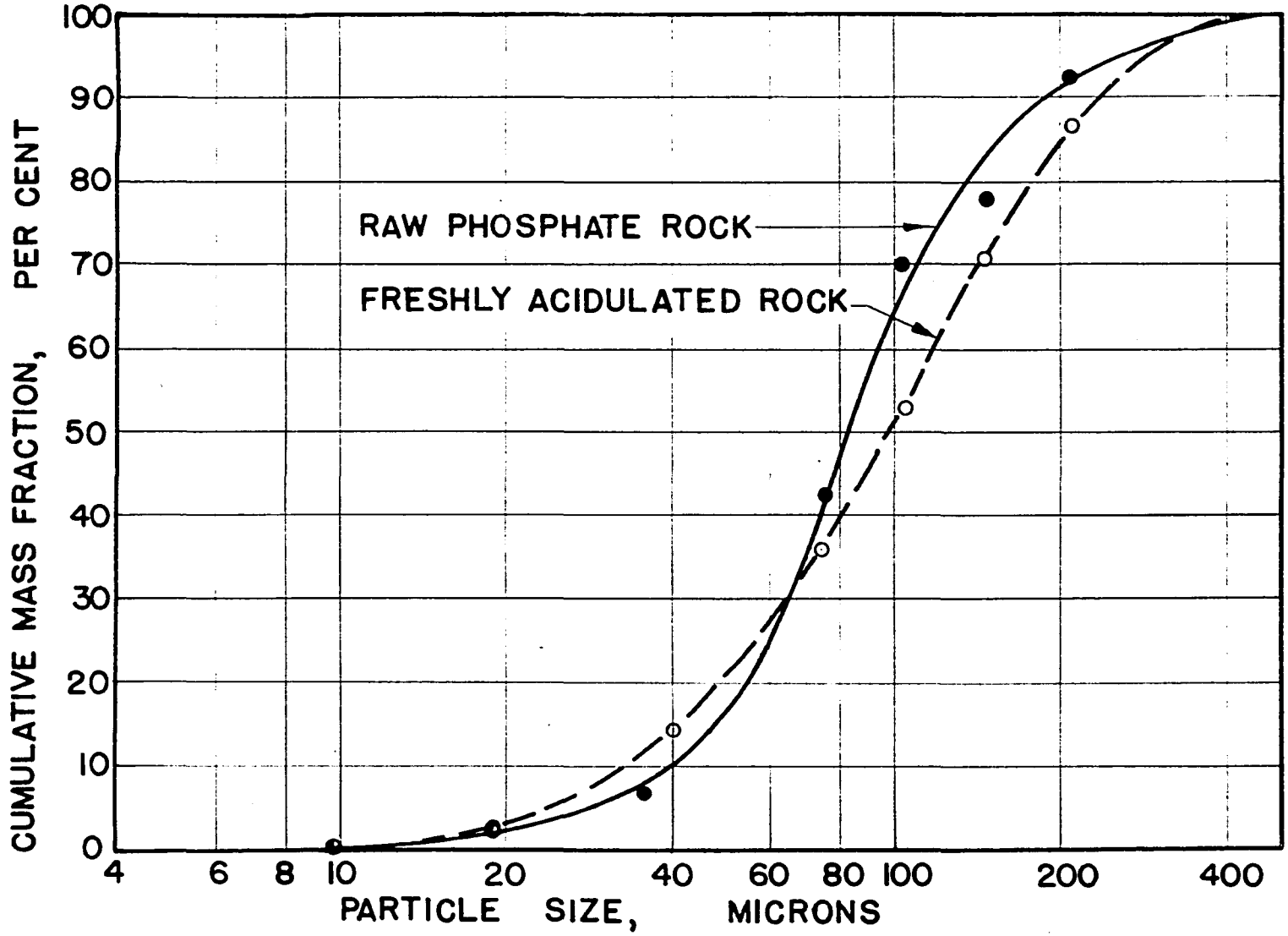

FIGURE 19. EFFECT OF ACIDULATION ON THE PARTICLE SIZE DISTRIBUTION OF PHOSPHATE ROCK

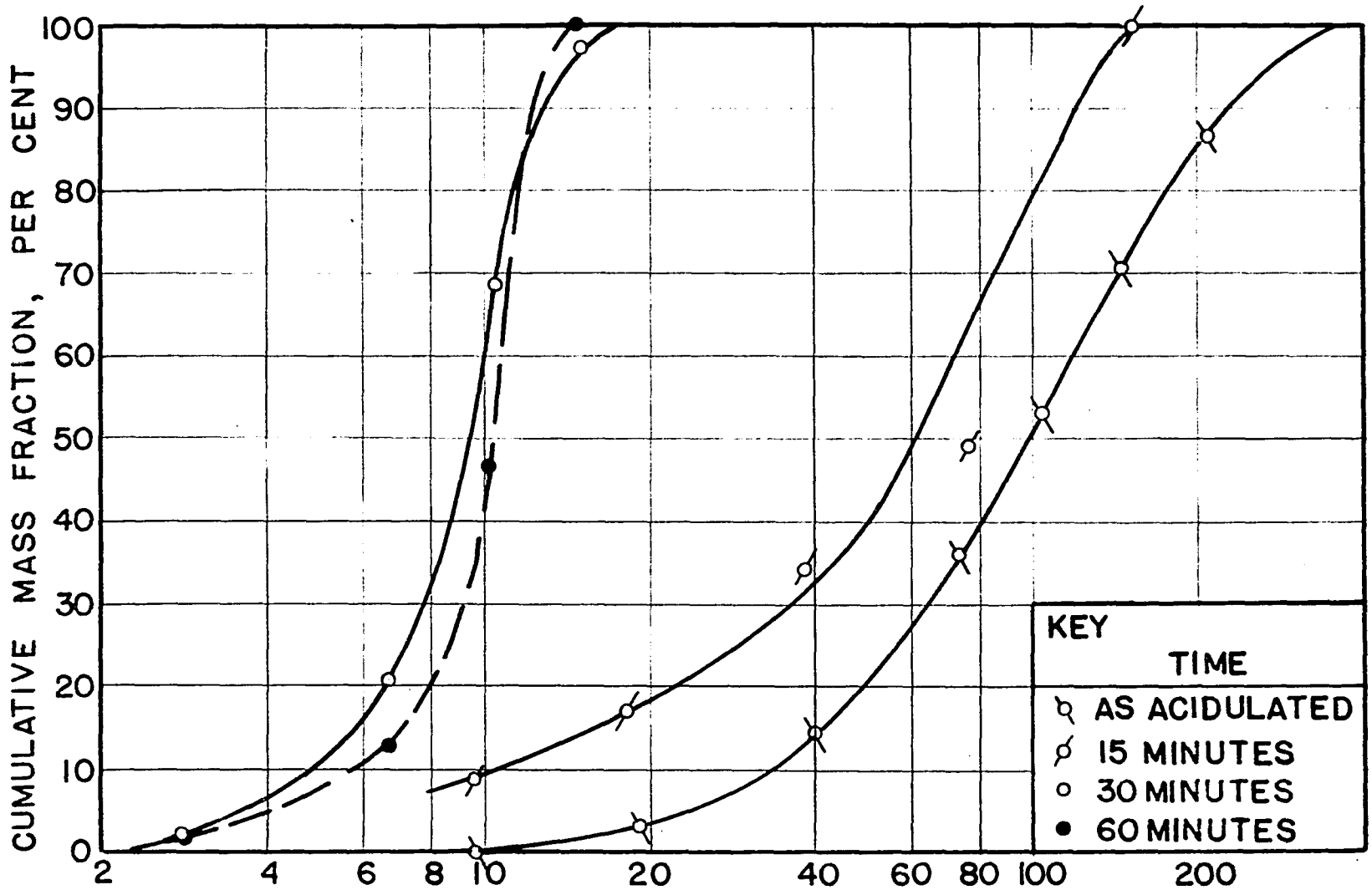

FIGURE 20. CHANGE IN PARTICLE SIZE DISTRIBUTION OF ACIDULATED PHOSPHATE ROCK WITH GRINDING TIME

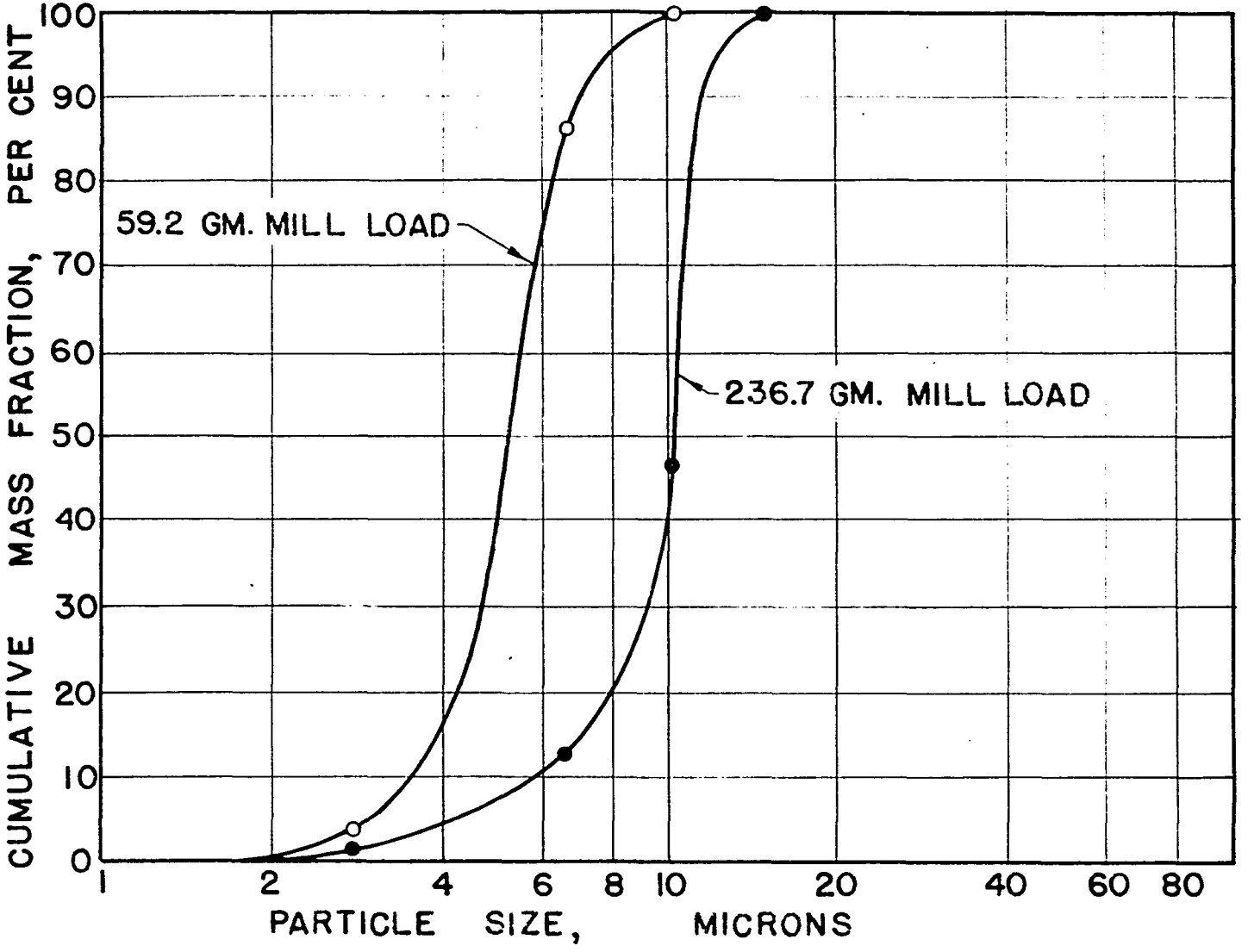

FIGURE 21. EFFECT OF MILL LOAD SIZE ON THE PARTICLE SIZE DISTRIBUTION AFTER GRINDING FOR 1 HOUR

particles were formed upon acidulation, they contributed very little to the total weight. Effective grinding apparently took place rapidly in the laboratory ball mill. The changes in distribution during grinding are shown in Figure 20. Grinding for longer than 30 minutes appeared to be unnecessary. Figure 21 shows the effect of a very small mill load (59.2 grams compared to a usual load of 236.7 grams) at a grinding time of one hour. Although further grinding was accomplished, its economy is doubtful.

APPENDIX C

Dicalcium Phosphate Formation

The use of an acidulation ratio of less than the usual 1.8 generally resulted in reduced conversion. Theoretically, some dicalcium phosphate should result instead of monocalcium phosphate according to the following equation:

$$Ca_{10}F_2(PO_4)_6 + 3H_2SO_4 \rightarrow 6CaHPO_4 + 3CaSO_4 + CaF_2$$

From this equation it may be seen that the acid required to produce dicalcium phosphate would be only one-half that required to produce monocalcium phosphate. In an attempt to promote this reaction, it was postulated that grinding during the acidulation in the laboratory ball mill would prevent $CaSO_4$ formation on the rock particles and allow the reaction to go to completion at low acidulation ratios. Thus, at an acidulation ratio of 0.7 the reaction could conceivably go to completion giving 100 per cent conversion.

Therefore, the effect of different operating conditions in the ball mill were investigated relative to the possible production of dicalcium phosphate. An acidulation ratio of 1.45 was used. The acid concentration and drying temperature were those previously determined by other workers at Iowa State College: that is, 35 per cent sulfuric acid and 185°C. drying chamber temperature. The variables studied were ball mill load and drying time. The results of these studies are given in Table 12.

Table 12. Data for the production of dicalcium phosphate

Run	Weight sample gms.	Drying time hrs.	Product analysis, per cent						
			Total P_2O_5	Water sol. P_2O_5	C.I. insol. P_2O_5	Water insol. P_2O_5	Avail. P_2O_5	Conv.	Moist.
14	236.7	1.00	23.1	8.5	4.2	10.4	18.9	81.9	
17	365.1	1.00	22.6	12.8	4.6	5.2	18.0	79.6	
26	118.4	0.50	23.8	9.2	5.6	8.2	17.4	75.7	1.5
27	59.2	0.50	22.4	6.8	4.4	11.2	18.0	80.4	
28	118.4	1.00	23.1	8.5	5.0	9.6	18.1	78.4	1.5
29	118.4	0.50	22.6	11.3	5.4	5.9	17.2	76.2	
31	59.2	0.50	21.0	9.2	3.8	8.0	17.2	81.9	
33	177.6	0.50	22.3	7.4	6.1	8.0	16.2	72.7	3.4
39	236.7	0.50	22.3	12.7	6.1	3.5	16.2	72.7	
42	236.7	0.50	22.4	14.6	5.0	3.8	17.4	77.6	2.3
43	118.4	1.00	23.0	9.2	5.4	8.4	17.6	76.5	
44	118.4	1.50	22.9	10.1	5.0	7.8	17.9	78.1	1.3
45	118.4	0.25	21.8	13.9	4.2	3.7	17.6	80.7	3.2
51	365.1	0.50	22.1	15.7	4.4	2.0	17.7	80.0	

These results are plotted in Figures 22 and 23. Phosphorus pentoxide conversion is used in these correlations as a synonym of availability which is the basis for the selling price of the fertilizer. The per cent water insoluble phosphorus pentoxide is a measure of the dicalcium phosphate content of the sample.

For 30 minutes drying time, the effect of the size of the mill load on the over-all phosphorus pentoxide conversion is plotted in Figure 22. Final conversion for all mill loads was low. The slightly increased conversion with small mill loads may be attributed to increased grinding action. The increased conversion at large mill loads appeared to be related to the drying rate. With a larger mill load the reduction of the fractional moisture content is slower than with a small mill load, other conditions being the same.

The possibility of higher final moisture contents being an important factor in the higher conversion with larger mill loads was considered. However, as shown in Figure 23, except at very high moistures and short drying times, the primary effect of increased drying time was to increase conversion slightly.

Many other combinations of drying temperatures and drying times were used but none gave phosphorus pentoxide conversions which were appreciably better.

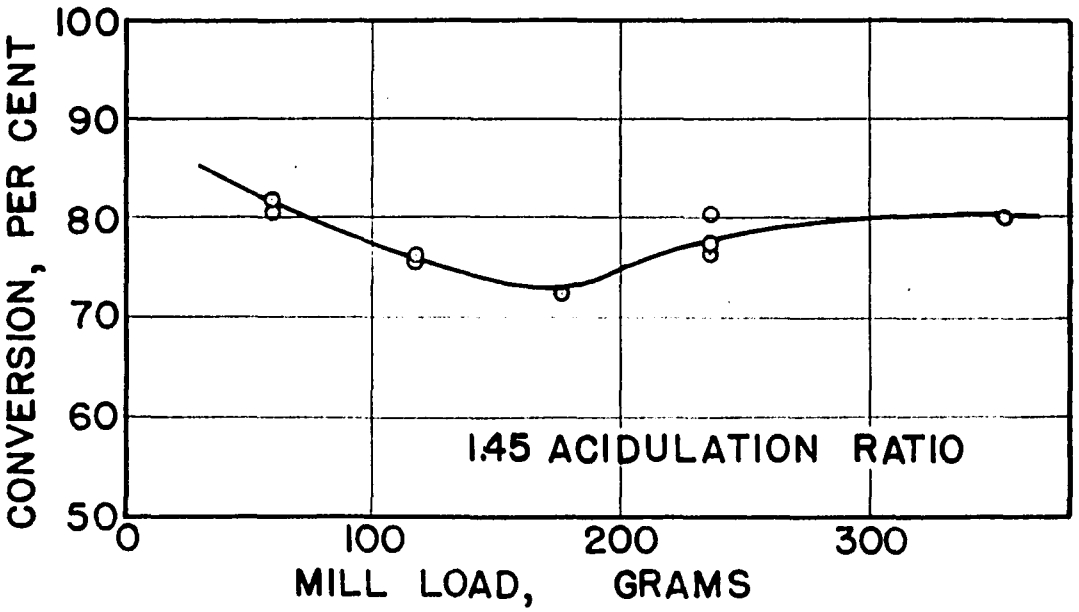

FIGURE 22. EFFECT OF MILL LOAD ON CONVERSION (30 MINUTES DRYING TIME)

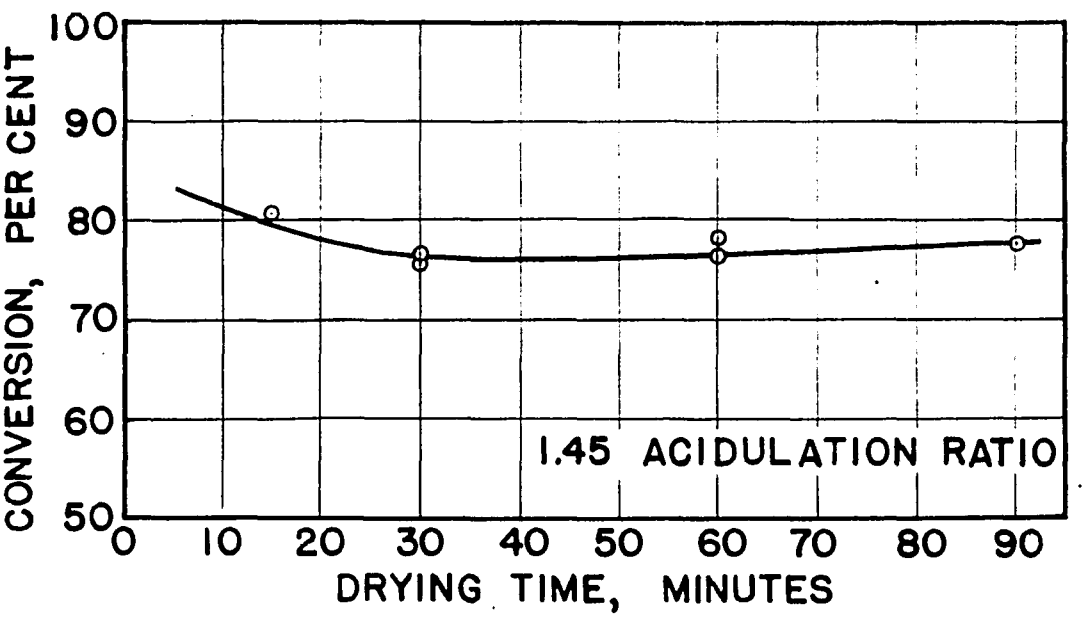

FIGURE 23. EFFECT OF DRYING TIME ON CONVERSION (118.4 GM. MILL LOAD)